STRUCTURAL STUDIES OF [4 + 2] PERHALOCYCLOPROPENE CYCLOADDUCTS

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
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UNIVERSITY OF FLORIDA

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To Phyllis and Will

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Robert Giles Posey

December, 1975

Chairman: Dr. Merle A. Battiste
Major Department: Chemistry

Previous literature reports of exclusive formation of endo [4 + 2] cycloadducts of perhalocyclopropenes with furan were shown to be in error by a single crystal X-ray structural analysis of the phenyl azide adduct 32 of 2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (20a), which revealed the exo stereochemistry of the gem-difluorocyclopropane ring in 32, and thus in 20a. Using exo-20a as a model compound, a series of chemical transformations were carried out in order to establish ^{1}H nmr and ^{19}F nmr parameters to be used for the determination of stereochemistry in unknown systems. In addition, heteronuclear decoupling, measurements of line widths at half-height ($W_{1/2}$), and $Eu(FOD)_3$ nmr shift experiments were carried out on 20a and

the series of compounds derived from 20a, of which all were known to possess exo stereochemistry.

New [4 + 2] cycloadducts of 1,2-dibromo-3,3-difluorocyclopropene (15) were prepared with 1,3-diphenylisobenzofuran, isobenzofuran, 6,6-diphenylfulvene, 6,6-dimethylfulvene, spiro[4.2 heptadiene, cyclopentadiene, and the acyclic diene 1-methoxy-1,3-butadiene. By the application of chemical transformations as well as the spectroscopic techniques previously mentioned, it was shown that under the reaction conditions used, the cyclic dienes formed exclusively exo [4 + 2] adducts with 15 as isolated products.

In the adducts of 15 with cyclopentadiene and spiro-[4.2]heptadiene (63 and 57a), substantial long range ^{19}F - ^{1}H coupling was observed in the ^{1}H and ^{19}F nmr spectra, and this phenomenon was part of the evidence used for the assignment of exo stereochemistry in these compounds. This $^{5}J_{FH}$ and $^{6}J_{FH}$ coupling was compared with previous literature reports, and in the case of the spiro[4.2]heptadiene adduct (57a) constitutes the first example of the intercalated mode of long range ^{19}F - ^{1}H coupling.

Having established the exo stereochemistry for the [4 + 2] cycloadducts of 15 formed at relatively high temperatures (80^{o} - 115^{o} C), the behavior of adduct 20a was examined at various temperatures. As a result, it was found that only exo-20a was formed at lower temperatures, but that at 75^{o} - 80^{o} C, an equilibrium mixture of exo-20a and endo-20 could be detected by ^{19}F nmr. The adduct of 15 with iso-

benzofuran was found by ^{19}F nmr to retain the original exo orientation after prolonged heating at 80° C.

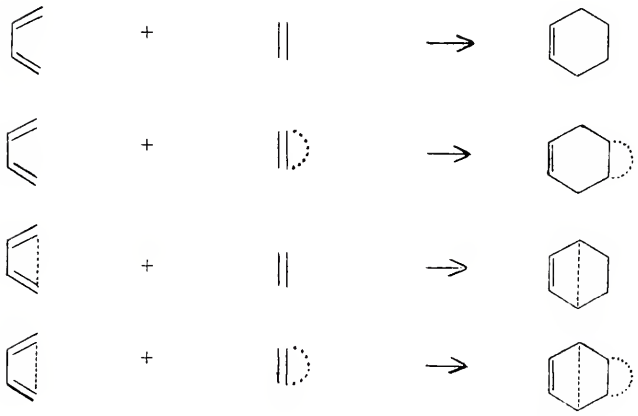
As part of the attempted synthesis of the epimeric exo (54)- and endo (55)-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]-octan-8-ones, the synthesis of the previously unknown 3,3-difluorocyclopropene (87) was attempted. In one such attempt, the product of the reaction of 15 with anthracene at 130° C was shown to be a ring opened species. In another attempt at the preparation of 87, the unstable 1,2-bis-(trimethylsilyl)3,3-difluorocyclopropene (86) was prepared, but the attempted conversion of 86 to 87 by hydrolysis failed to give any volatile products.

CHAPTER I

INTRODUCTION

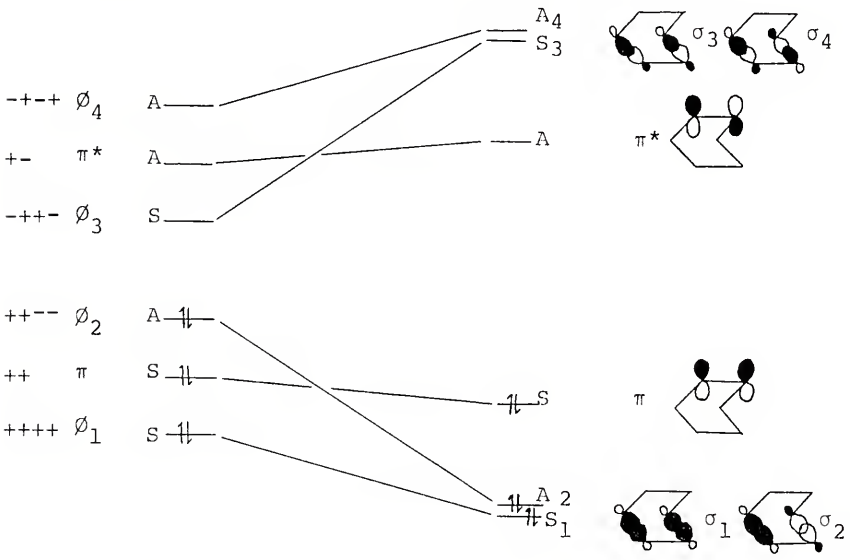
Diels-Alder Reactions - General

Reactions between conjugated dienes and olefins have been thoroughly investigated and have become quite important synthetic tools in organic chemistry.[1] The reaction products are either mono-, bi-, or tri-cyclic, depending on whether the diene and/or dienophile are cyclic or acyclic, as shown below.



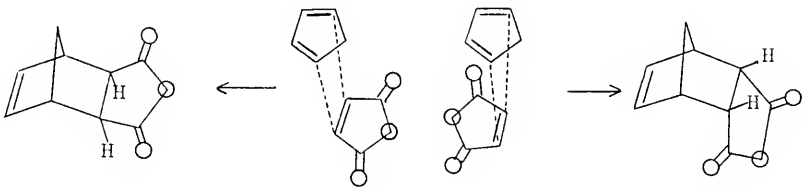
Such reactions were first extensively utilized by Diels and Alder, beginning in 1928,[2] and since then the mechanistic aspects of the Diels-Alder reaction have been probed by a number of workers.[3] Various effects of substituents,

catalysts, and solvents as well as steric and electronic factors were reviewed by Seltzer.[3] Of course, the Diels-Alder reaction may be viewed in terms of the Woodward-Hoffmann orbital symmetry treatment.[4] As illustrated in the following correlation diagram, Diels-Alder cycloadditions are thermally allowed processes, with the likelihood of reaction and structure of products controlled by substituents on both the diene and the dienophile.



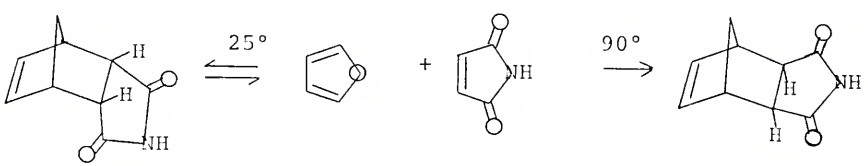
In those Diels-Alder reactions where the possibility of stereoisomerism exists, predetermination of reaction product stereochemistry is not always as simple as merely applying the Alder endo rule.[5] This rule states that the reacting species, when arranged in parallel planes, will react via the orientation which has the "maximum accumulation" of double bonds, which includes all double bonds in

both the diene and the dienophile. The endo-addition rule is illustrated below for the reaction of maleic anhydride with cyclopentadiene, which proceeds to give > 98.5% endo-adduct and <1.5% exo-adduct.[6] Indeed, the majority of



<1.5% >98.5%

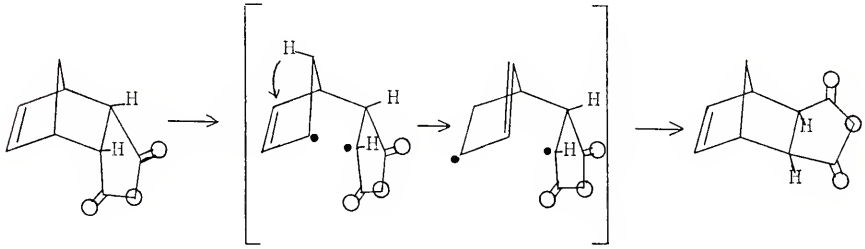
cycloadditions between cyclic dienes and cyclic dienophiles obey the endo-addition rule. However, the endo-addition rule is applicable to kinetically controlled phenomena, and does not necessarily reflect the relative thermodynamic stabilities of stereoisomeric products. In the example shown below, the endo-adduct of furan and succinimide isomerizes upon warming to the more thermodynamically stable exo isomer.[7] Analagous behavior, i.e., facile cycloreversion



of the endo isomer followed by addition to give the

thermodynamically preferred exo isomer has also been reported for adducts of fulvenes.[8]

The question of mechanistic pathways for endo/exo isomerizations of Diels-Alder adducts has been examined in a variety of diene/dienophile systems, and several possible mechanisms have been proposed for observed endo to exo isomerizations. The first of these possibilities, and the one most universally applicable is a retro-Diels-Alder reaction followed by subsequent recombination to form the thermodynamically more stable product.[9] However, in some systems intramolecular endo to exo isomerizations can occur by a one bond cleavage-hydrogen shift mechanism.[9]



A third mechanism formulated by Berson et al.,[10] for the isomerization depicted above is a process involving dissociation of the endo adduct to the endo-addition complex, which through rotation isomerizes to the exo-addition complex, followed by rapid recombination to give a net "internal" isomerization. However, this mechanism has not been firmly established, and has been challenged by other authors.[11] Also, Berson and his co-workers attempted to

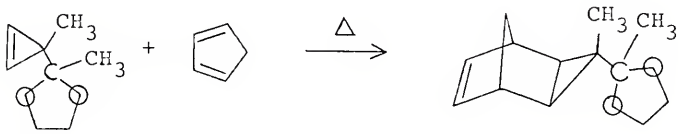
obtain evidence for their internal isomerization mechanism in two other systems,[12,13,14] but the data obtained best support the retro-Diels-Alder-recyclization mechanism.

Alkyl- and Aryl-Cyclopropenes as Dienophiles

A special case of the Diels-Alder reaction involves utilization of cyclopropenes as dienophiles. Cyclopropene itself reacts at 0^{o} C with cyclopentadiene to form only endo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.[15] The corresponding exo-alkene had been prepared from bicyclo[2.2.1]hepta-2,6-diene by Simmons and Smith using methylene iodide in the presence of zinc/copper couple.[16] Cyclopropene also reacts with 6,6-dimethylfulvene to form only an endo Diels-Alder adduct,[17] and this cycloaddition offers a convenient synthetic pathway into the endo-tricyclo[3.2.1.$0^{2,4}$]octyl ring system. Subsequently, the reaction of 6,6-dimethyl-(or 6,6-diphenyl)-fulvene with 1,2,3-triphenylcyclopropene was reported by Martin[18] to give a 1:1 adduct. However, careful ^{1}H nmr analysis indicated that the adduct had the exo structure.

Cyclopentadiene also forms endo-syn-3-methyltricyclo-[3.2.1.$0^{2,4}$]oct-6-ene with 3-methylcyclopropene.[19,20] Similarly, 1,2-diphenylcyclopropene,[21] 1,2,3-triphenylcyclopropene,[21] 1,2-diphenylcyclopropene-3-carboxylic acid,[21] and 1,2-diphenylcyclopropene-3-carboxylic acid methyl ester[21] all form endo 1:1 adducts with cyclopentadiene at room temperature . Curiously, 3,3-dimethylcyclopropene does not react with cyclopentadiene even at 100^{o} C,[20] presumably due

to large steric interactions of the geminal methyl groups with the cyclopentadiene molecule in the transition state. It is evident that such interactions are sufficient to inhibit adduction in either the exo or the endo mode. If, however, forcing conditions are used, sterically inhibited reactions can be carried out, as in the case of the reaction of cyclopentadiene with 3-acetyl-3-methylcyclopropene ethyleneketal (1) at 140° C for 12 hours.[19] The adduct so obtained was shown, by chemical conversion to a known compound, to have an exo structure. Even more anomalous was the behavior of the ketone, 3-acetyl-3-methylcyclopropene (2), which at 140° C apparently rearranges to 1-methyl-3-acetylcyclopropene (3) before adduction with cyclopentadiene to give endo-anti-2-methyl-3-acetyl-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, as shown below.



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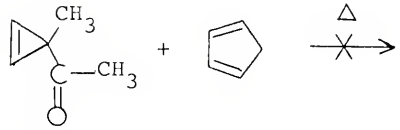
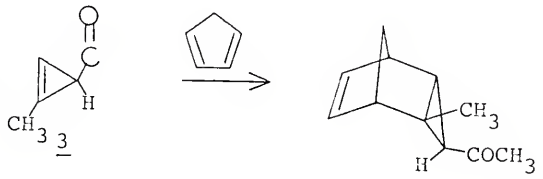


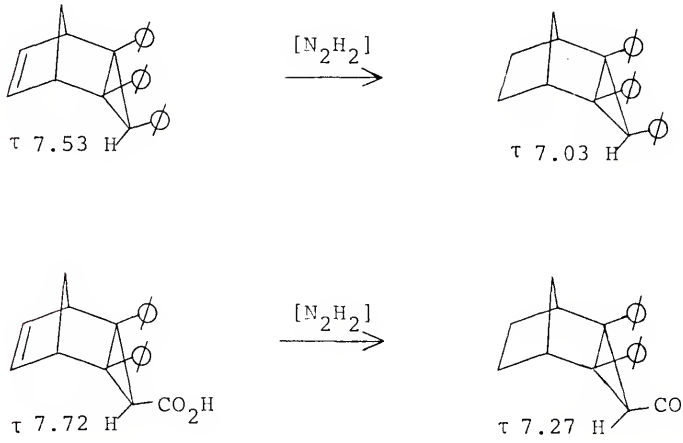
2 → 3



The use of dienes other than cyclopentadiene in Diels-Alder reactions of cyclopropenes has produced some strikingly different results from the standpoint of the stereochemistry of [4 + 2] adducts. Indeed, the predominant stereochemistry of adducts produced in reactions of alkyl- and aryl-cyclopropenes with furan is exo. Cyclopropene reacts with furan to give a 1:1 mixture of exo- and endo-8-exatricyclo[2.2.1.$0^{2,4}$]-oct-6-ene.[22,23] When 1,3-diphenylisobenzofuran is the diene component, exo products are obtained with cyclopropene,[24] 1-methylcyclopropene,[24] 1,2-diphenylcyclopropene,[25] and 1,2,3-triphenylcyclopropene.[21] After 3 days in refluxing xylene, tetraphenylcyclopropene and 1,3-diphenylisobenzofuran showed no signs of reacting,[21] but 3-methyl-1,2,3-triphenylcyclopropene under the same conditions gave after 3 days 3-methyl-1,2,3,4,5-pentaphenyl-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-ene[21,24] (albeit in only 8% yield). This behavior by a tetra-substituted cyclopropene is in sharp contrast to the findings using cyclopentadiene, which were discussed above. Clearly then, the steric and electronic factors controlling the stereochemistry of addition as well as the reactivity on Diels-Alder reactions of cyclopropenes vary considerably between cyclopentadiene and furan or 1,3-diphenylisobenzofuran.

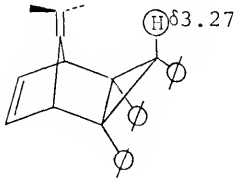
It is instructive to examine the evidence used by the various investigators to evoke either exo or endo stereochemistry for [4 + 2] cycloadducts of alkyl- and aryl-cyclopropenes. In some cases stereochemical assignments are based on comparisons to known compounds[15,16,17,20] and in others ^{1}H

nmr data are used to make the assignments.[21,22,23,24,25] The adducts of cyclopentadiene with 1,2,3-triphenylcyclopropene and 1,2-diphenylcyclopropene-3-carboxylic acid were ascribed endo configurations based on the chemical shift of the lone cyclopropyl proton, which in either case appears at higher field than expected due to shielding by the C=C double bond. When both adducts were reduced to the saturated compounds with diimide, the cyclopropyl proton signal is shifted downfield by approximately 0.5 ppm, as shown below.



An analagous argument was used by Martin[18] to settle the question of stereochemistry in the 6,6-dimethylfulvene adduct (4) of 1,2,3-triphenylcyclopropene. Comparison of the chemical shift values of the cyclopropyl benzylic proton in this adduct with the same proton in the exo-anti-

(5) and the endo-anti-(6)-2,3,4-triphenyltricyclo[3.2.1.$0^{2,4}$]-oct-6-enes pointed to the exo structure of the fulvene adduct, as shown below.



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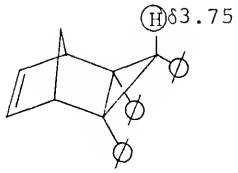

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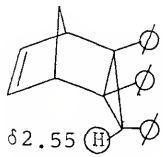

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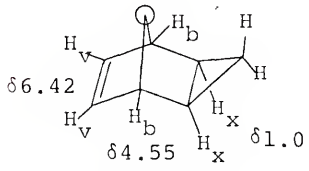
Turning to the adducts of furan[22,23] and 1,3-diphenylisobenzofuran,[24,25] ^{1}H nmr prarmeters have once again been used to elucidate stereochemistry. The reaction of cyclopropene with furan produces a 1:1 mixture of the exo(7)- and endo(8)- adducts. In the exo case, no significant coupling is observed between the bridgehead protons H_b and the cyclopropyl methine protons H_x. However, in the endo adduct, the ^{1}H nmr spectrum indicates substantial H_b-H_x coupling. The cyclopropene adduct[24] (9) and the 1,2-diphenyl-



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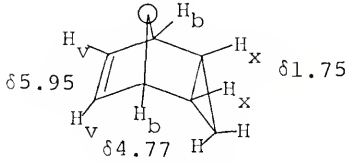
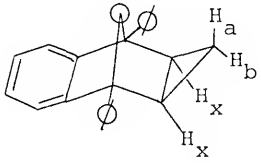


8

cyclopropene adduct[25] (10) of 1,3-diphenylisobenzofuran were both assigned exo structures based on the observed chemical shifts of their cyclopropyl protons syn to the oxygen bridge in either case. This type of proton is subject to steric deshielding by the lone electron pairs on the oxygen. Shown below are the chemical shifts, multiplicities, and observed coupling constants for 9 and 10.



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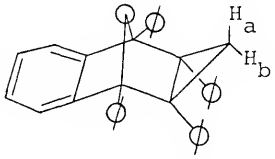


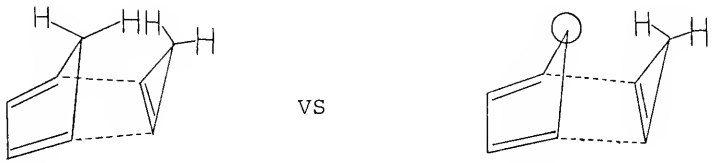
10

	δ	(mult)	J(Hz)
H_a	1.84	(d of t)	J_{ab}= 5.2
H_b	0.84		J_{ax}= 3.7
H_x	1.62	(d of d)	J_{bx}= 6.74

	δ	(mult)	J(Hz)
H_a	2.94	(d)	J_{ab}= 4.7
H_b	1.80	(d)	

Thus, it would seem that by careful consideration of ^1H nmr data obtained for Diels-Alder adducts of alkyl- and aryl-cyclopropenes, it is possible to make definitive exo of endo structural assignments with a reasonable degree of certainty.

The task of rationalizing why these cycloadditions of furan and 1,3-diphenylisobenzofuran give exo products in variance to the Alder rule[5] is no less difficult than ascertaining the correct stereochemistry of the adducts. LaRochelle and Trost[22] advanced such an explanation based on the transition state structures for exo and endo adduction. They envisaged an exo transition state as being distinctly like a boat cyclohexane (as shown below), and thus subject to destabilization by 1,3 "flagpole" interactions, which could be substantial in those cases where the diene is cyclopentadiene. When the $-CH_2-$ of cyclopentadiene is replaced by -O- (furan or 1,3-diphenylisobenzofuran), the 1,4 steric interactions in the exo transition state are evidently reduced enough to enable the reaction to proceed to give exo products. However, it must

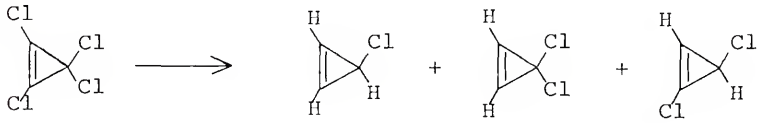


be pointed out that although this transition state argument seems to adequately explain the results of the Diels-Alder reactions of alkyl- and aryl-cyclopropenes, it obviously does not take into consideration electronic factors and other steric interactions in the transition state which may

also be substantial enough to affect the exo/endo ratio of products.

Halocyclopropenes as Dienophiles

Armed with the knowledge that alkyl- and aryl-cyclopropenes undergo Diels-Alder reactions with acyclic and cyclic 1,3-dienes, several authors undertook investigations directed towards the synthesis of and Diels-Alder reactions of halogenated cyclopropenes. Since 1963, several thermally stable halogenated cyclopropenes have been synthesized. In that year, Tobey and West reported the dehydrohalogenation of pentachlorocyclopropane in 18M aqueous KOH to give tetrachlorocyclopropene (11),[26,27] which these same authors subsequently employed as the starting material for tetrabromocyclopropene (12), 3-fluoro-1,2,3-trichlorocyclopropene (13), 1,2-dichloro-3,3-difluorocyclopropene (14), and 1,2-dibromo-3,3-difluorocyclopropene (15).[28] Reduction of 11 with tri-n-butyltin hydride as reported by Breslow et al.[29] affords a mixture of 3-chlorocyclopropene (59%), 3,3-dichlorocyclopropene (14%), and 1,3-dichlorocyclopropene (27%). In 1969,



11

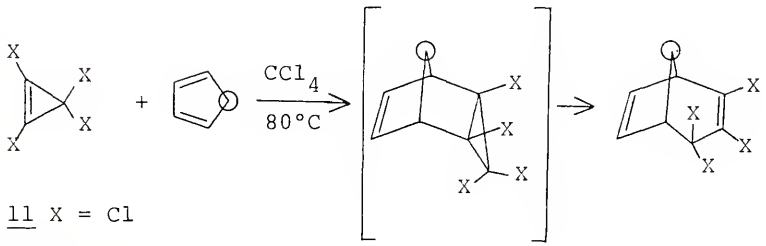
Sargeant and Krespan reported the successful synthesis of perfluorocyclopropene (16),[30] as well as the duplication of

the synthesis previously reported of 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (17).[31,32] Other reported gem-difluorocyclopropenes include some 1-(perfluoroalkyl)-3,3-difluorocyclopropenes[33] and some steroid derivatives incorporating a gem-difluorocyclopropene moiety.[34]

Since many of the cyclopropenes mentioned above are thermally stable and relatively high boiling, several authors have taken advantage of these properties to prepare [4 + 2] cycloadducts with a variety of cyclic and acyclic dienes. Since the structural assignments of these adducts rests on conclusions drawn from spectral data, these data will be closely examined. Also, due to the subtle differences observed in the spectra for pairs of stereoisomers, such differences will be discussed in terms of their relevance to making structural assignments.

The most widely reported perhalocyclopropene to be used as a dienophile is tetrachlorocyclopropene (11), which forms 1:1 adducts with furan,[35,36] 13,14-dioxatricyclo-[8.2.1.$1^{4,7}$]tetradec-4,6,10,12-tetraene,[37], 1,3-diphenylisobenzofuran,[24,38] cyclopentadiene,[35] and the acyclic dienes 1,3-butadiene,[35] and trans,trans-1,4-diphenyl-1,3-butadiene.[39] The observed ring opened product of 11 with furan was envisaged by Law and Tobey to arise through an initially formed endo tricyclic adduct, which at the reaction temperature (80°C) undergoes facile ring opening to 2,3,4,4-tetrachloro-8-oxabicyclo[3.2.1]-octa-2,6-diene. Completely analagous behavior was observed for tetrabromocyclopropene (12), as

shown below. These authors based their conclusion that the



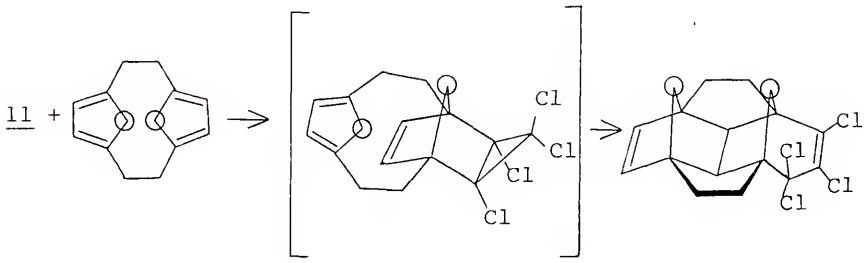
11 X = Cl

12 X = Br

initially formed [4 + 2] adduct was endo on transition state calculations carried out by Herndon and Hall[40] on the cyclopentadiene dimerization, and transition state steric arguments for the system shown above. An interesting alternative mechanism for the above reaction was considered by Magid and Wilson,[36] which involved ionization of a labile methylene Cl in 11 to form the trichlorocyclopropenium cation, which subsequently formed an ionic cycloadduct with furan, followed by rapid ring opening and capture by Cl^- to yield the observed product. However, their kinetic data obtained from the reaction using cyclopentadiene as the diene instead of furan, as well as stereochemical studies,[36] precluded adoption of this ionic mechanism in that the data were more consistent with the direct cycloaddition mechanism.

A contrasting opinion of the stereochemical mode of tetrachlorocyclopropene (11) cycloadditions was advanced in 1971 by Battiste et al.,[37] who suggested that the initial reaction of 11 with the [2,2] (2,5)-furanophane shown below occurs to give the exo adduct, which undergoes further

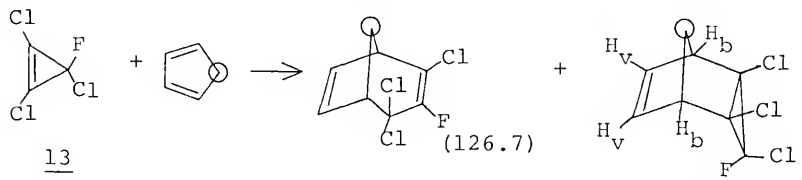
reactions. These authors cited the analagous reactions of



furan and 1,3-diphenylisobenzofuran discussed above[22,29] as the basis for their supposition. Since it is impossible to obtain absolutely reliable stereochemical information from spectroscopy alone for adducts of tetrachlorocyclopropene (11), other means must be sought for accurate structure determinations. In this vein, Bordner and Howard,[38] in collaboration with Magid and Wilson,[36] have recently conducted a single crystal X-ray analysis of the adduct of 11 with 1,3-diphenylisobenzofuran, which revealed that the adduct is unquestionably exo, thus lending support to the contention that perhalocyclopropene Diels-Alder reactions may in fact proceed in the exo, or "anti-Alder" manner.

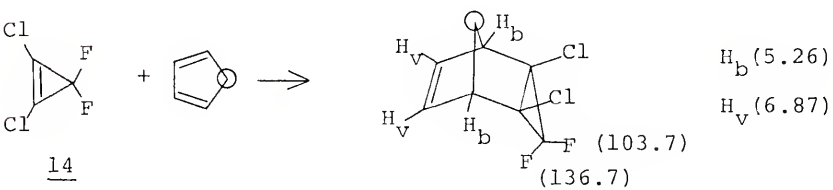
When one or both of the geminal positions of a perhalocyclopropene are substituted with fluorine, the mono- or gem-di-fluorocyclopropenes, when reacted with a diene, form the corresponding fluorinated cyclopropanes, which in many cases are stable to ring opening at the reaction temperature due to the inherent strength of the C-F bond. The fluorinated cyclopropenes that have been studied as dienophiles have been

synthesized principally by Tobey et al.,[28,35] and Sargeant.[30,31] Tetrachlorocyclopropene (11), when treated with SbF_3, forms a separable mixture of 1,2,3-trichloro-3-fluorocyclopropene (13) and 1,2-dichloro-3,3-difluorocyclopropene (14). Tetrabromocyclopropene (12), when subjected to treatment with SbF_3 at somewhat higher temperatures forms a single product, 1,2-dibromo-3,3-difluorocyclopropene (15). Diels-Alder adducts with furan for all



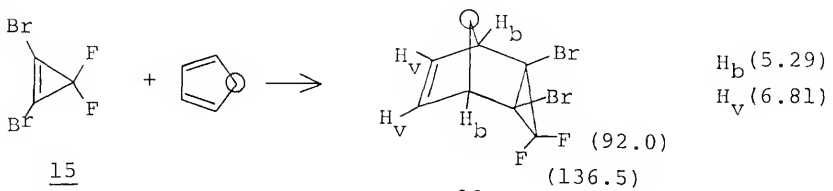
13 18

H_b(5.30)
H_v(6.83)



14 19

H_b(5.26)
H_v(6.87)

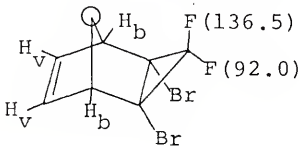


15 20

H_b(5.29)
H_v(6.81)

three of these fluorocyclopropenes were first prepared in 1968 by Law and Tobey[35] and were assigned the structures shown above. The ^{1}H nmr chemical shifts are in δ relative to TMS, and the ^{19}F nmr chemical shifts are in δ upfield from $CFCl_3$. All shift values shown are as reported by Law and Tobey, and the assignments are their own.

Close inspection of the nmr data for the tricyclic compounds 18, 19, and 20 reveals some interesting features. First, a fluorine cis to either Br or Cl has a signal at lower field than a trans fluorine. Note that in the monofluorinated compound (18), the single ^{19}F resonance may be assigned with reasonable certainty to a fluorine trans to the two bridgehead Cl atoms. Also, the δ values indicate more efficient deshielding by a cis Br than a cis Cl, as expected. Second, in both of the gem-difluoro compounds, (19) and (20), only one fluorine, the fluorine trans to either Br or Cl and at highest field, is coupled to H_b (J = 2 Hz). The single fluorine resonance of the monofluoro compound (18) also appears as a triplet (J = 2.5 Hz), thus supporting the other assignments. Tobey and Law in 1968, with Magid and Wilson concurring in 1971, therefore assigned the endo structures to 18, 19, and 20 as shown above. However, if all three structures are considered to be exo, the



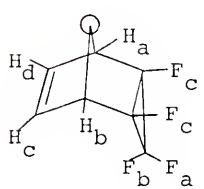
H_b(5.29)
H_v(6.81)

"20a"

nmr data can be made to "fit" equally well, as shown above taking 20 as an example. In accordance with the criteria established above, in the now exo 20a, the lowest field fluorine is cis to the two Br atoms, and the higher field fluorine is coupled to H_b and appears as a doublet of triplets (J_{FF} = 144 Hz, J_{FH_b} = 2 Hz). Tobey and Law argued that in 20, the high field fluorine is shielded by the C=C double bond since this adduct was thought to be endo. This argument is not justified, since the same shielding arguments that are well established for ^1H nmr cannot be applied to ^{19}F nmr.[41] This is particularly so in the compounds in question, due to the lack of data for suitable model compounds. Two other furan adducts of gem-difluorocyclopropenes have been reported by Sargeant.[31] Tetrafluorocyclopropene (16) and 1,2-bis(trifluoromethyl)3,3-difluorocyclopropene (17) form 1:1 furan adducts, 21 and 22, respectively, at room temperature, both of which are shown in Table I with the structural and nmr spectral assignments as made by Sargeant.

Table I

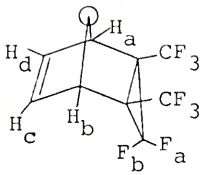
^1H and ^{19}F nmr Data for 21 and 22



21

	δppm	mult.	splittings, Hz	assign.	J,Hz
	δH				
	6.32	M	W_b ~ 4	c,d	F_aF_b=
	4.60	2 X M	3.4, W_b ~ 8	a,b	175
	δF				F_bF_c=
	129.9	2	0.3	F_b	0.0
	139.3	3 X 3	23.3,3.2	F_a	23.4
	227.8	2	23.4	F_c	$H_{a,b}F_a$=3.2

Table I - Continued



22

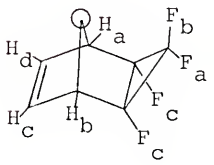
δppm	mult.	splittings, Hz	assign.	J,Hz
δH				
6.62	1	$W_{1/2}$ ~ 3.8	c,d	CF_3F_a=
5.17	1	$W_{1/2}$ ~ 3.8	a,b	16
δF				CF_3F_b=
59.7	2 X 2	16, 2.2	CF_3	2.2
116.7	7	15.9	F_a	F_aF_b=
137.0	7 X 3	2.2, 1.2	F_b	166
				$H_{a,b}F_b$=
				1.2

A detailed comparison of the nmr spectra for 21 and 22 with data accrued earlier for similar compounds does not, in fact, lend support to the structures shown above, as discrepancies can be noted. First, compared to the previously discussed compounds, F_a and F_b in Sargeant's tetrafluorocyclopropene adduct (21) would seem to have their assignments reversed, were it not for the large (23.3 Hz) coupling between F_c and F_a, which allows unambiguous assignment of F_a to the signal at δ139.3. Secondly, if 21 were actually endo, one would expect to see substantial coupling from $H_{a,b}$ to F_c, which should be as large, if not larger, than the ^1H - ^1H coupling observed for bridgehead proton ($H_{a,b}$) - exo - H_2, H_4 interactions.[20, 21,42,43] No such coupling is reported for 21 and no $W_{1/2}$ data were cited for the F_c doublet. The anomalies

within the ^{1}H and ^{19}F nmr data require that the alternate exo structure 21a be considered. To this end, 21a, the revised exo structure, accompanied by the reassignments for the ^{1}H and ^{19}F nmr spectra, are illustrated in Table II. Even though this structure eliminates the problem of

Table II

^{1}H and ^{19}F nmr Data for 21a



21a

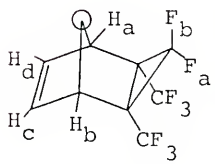
δppm	mult.	splittings, Hz	assign.	J,Hz
δH				F_aF_b=
6.32	M	W_b ~ 4	c,d	175
4.60	2 X M	3.4, W_b ~ 8	a,b	F_bF_c=
δF				0.0
129.9	2	0.3	F_b	F_aF_c=
139.3	3 X 3	23.3, 3.2	F_a	23.4
227.8	2	23.4	F_c	$F_aH_{a,b}$(?)=
				3.2

no observed $J_{H_{a,b}F_c}$ (since bridgehead-H/endo-H coupling is usually negligible),[42] the chemical shift values as assigned here do not agree with the previously observed[35] appearance of the geminal fluorine cis to $C_{21}C_4$ cyclopropyl halogens at lower field than the trans geminal fluorine. Thus, it would seem that in the absence of other data to resolve the paradox, such as heteronuclear decoupling results, the assertion by Sargeant that "the stereochemistry [of 21] cannot be assigned with certainty" must remain unchanged.

Re-evaluation of the structure of the 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene adduct 22 in the same fashion (that is, as the exo adduct 22a), may prove more productive than in the case of 21. Once again, fitting the observed ^{1}H and ^{19}F nmr data to 22a, one obtains the results shown in Table III. Of interest here

Table III

^{1}H and ^{19}F nmr Data for 22a



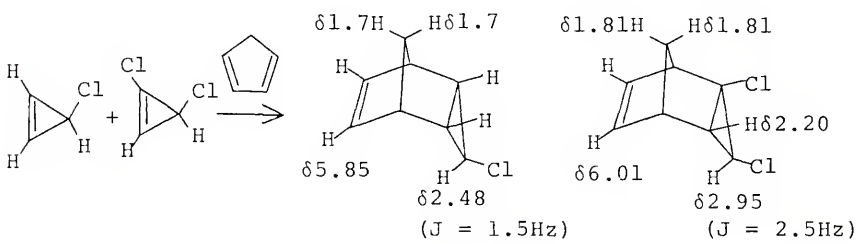
22a

	δppm	mult.	splittings, Hz	assign.	J,Hz
	δH				CF_3F_a=
	6.62	1	$W_{1/2}$ ~ 3.8	c,d	16
	5.17	1	$W_{1/2}$ ~ 3.8	a,b	CF_3F_b=
	δF				2.2
	59.7	2 X 2	16, 2.2	CF_3	F_aF_b=
	116.7	7	15.9	F_a	166
	137.0	7 X 3	2.2, 1.2	F_b	$H_{a,b}F_b$=
					1.2

is the value for F_b, which in this case is rather close to the value for F_b in Tobey and Law's furan adduct of 15. The spectral data for that adduct (20a) were likewise argued to be consistent with exo stereochemistry (see p 17). In addition, the assignment of F_a to the lower field signal is in line with the previously discussed trend. In fairness, however, either the exo structure 22a or the endo structure 22 can be fitted to the data, as Sargeant readily acknowledged.[31]

Thus, if the structure of one of these furan Diels-Alder adducts could be established concretely, the development of diagnostic techniques applicable to other compounds of this type might be in the offing.

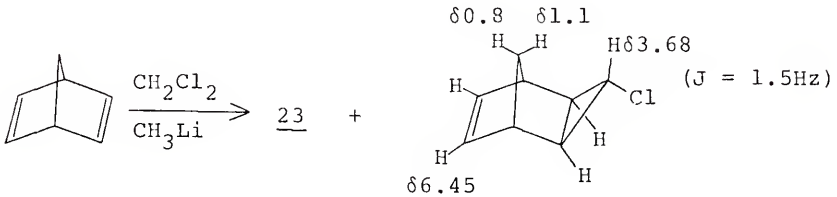
The problem of correctly assigning stereochemistry in halocyclopropene adducts is further confounded by the existence of a body of data for cyclopentadiene adducts of other halocyclopropenes. One such study by Magid and Wilson[36] dealt with cyclopentadiene adducts formed by reaction of excess cyclopentadiene with a mixture of 3-chlorocyclopropene, 3,3-dichlorocyclopropene, and 1,3-dichlorocyclopropene.[29,36] Curiously, these authors did not report formation of an adduct from the 3,3-dichloro-cyclopropene. However, the remaining cyclopropenes afford 1:1 adducts 23 and 24, both of which appear to be exclusively endo, as shown below with the appropriate ^{1}H nmr data. Other evidence for structures 23 and 24 was obtained from the



23 24

reaction of norbornadiene with chlorocarbenoid, which yielded

the monochloro endo-anti compound 23 as well as the exo-anti isomer 25 shown below with its ^{1}H nmr data. (That



25

26% 74%

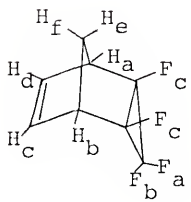
carbene additions to bicyclic systems such as norbornadiene proceed to give preferentially exo addition products has been well documented,[43,44] and will be discussed later.) Finally, reduction of 23 by sodium in tert-butyl alcohol produced only the known endo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.

Other than the ring opened adducts of tetrabromocyclopropene (12) and tetrachlorocyclopropene (11) prepared by Law and Tobey,[35] only two other halogenated cyclopropenes have been treated with cyclopentadiene, namely 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (17) and tetrafluorocyclopropene (16), as reported by Sargeant.[31] Cyclopentadiene when reacted at room temperature for 24 hours with 16 gave only 2,3,3,4-tetrafluorotricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (26), but the bis(trifluoromethyl) compound 17 gave two products, 27 and 28, in 90% yield in a 69:31 ratio. Once again, all three of these compounds with the nmr data

as reported and assigned by Sargeant are shown in Table IV.

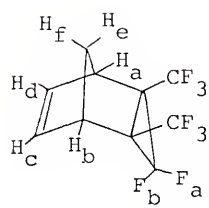
Table IV

^{1}H and ^{19}F nmr Data for 26, 27, and 28



26

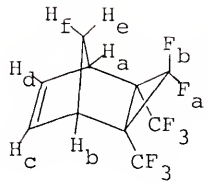
δppm	mult.	splittings, Hz	assign.	J,Hz
δH				H_eH_f=10.5
6.71	3	1.4	c,d	H_eF_c=6.3
3.23	7	1.8, W_b ~ 14	a,b	F_aF_b=177
1.75	M	$W_{1/2}$ ~ 4.5	f	$F_aH_{c,d}$=1.8
1.19	M (3X3X2)	6.0, 2.1, 2.1	e	F_aF_c=24.3
δF				$F_aH_{a,b}$=4.3
128.1	7	0.4, $W_{1/2}$ ~ 6	F_b	$F_cH_{a,b}$=2.3
134.8	M (3X3X3)	24.3, 4.3, 1.8	F_a	F_bF_c=1.4
221.0	M (2X2X3 X2)	24.4, 6.3, 2.3, and 1.4	F_c	



27

δH				H_eH_f=8.6
6.72	1	$W_{1/2}$ ~ 5.5	c,d	F_aCF_3=19.0
3.57	1	$W_{1/2}$ ~ 6.5	a,b	F_bCF_3=2.6
2.01	1	$W_{1/2}$ ~ 4	f	F_aF_b=178
1.15	1	$W_{1/2}$ ~ 8	e	$H_?F_b$=2.8
δF				
59.9	2 X 2	19.0, 2.6	CF_3	
113.7	7	19.0	F_a	
129.9	2 X 7	2.8, 2.6	F_b	

Table IV - Continued

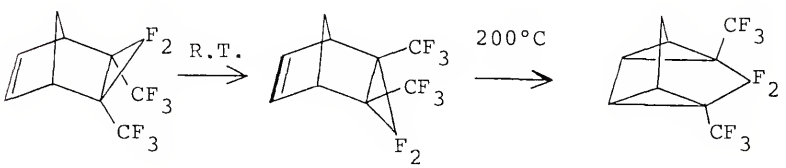


28

δppm	mult.	splittings, Hz	assign.	J,Hz
δH				H_eH_f=8.4
6.27	2 X 3	3.2, 2.0	c,d	CF_3F_a=19.0
3.57	1	$W_{1/2}$ ~ 6.5	a,b	CF_3F_b=2.6
2.36	1	$W_{1/2}$ ~ 5	e	F_aF_b=177
1.84	1	$W_{1/2}$ ~ 7	f	$H_?F_a$=8.5
δF				
61.7	2 X 2	19.0, 2.6	CF_3	
109.4	7 X 2	19.0, 8.5	F_a	
136.0	7	2.6	F_b	

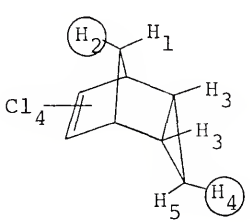
The assignments of stereochemistry in 27 and 28 as well as some of the nmr chemical shift assignments are somewhat suspect, and it becomes necessary at this point to indicate several anomalies in Sargeant's proposed structures. First, on chemical grounds, one would expect both tetrafluorocyclopropene (16) as well as 1,2-bis-(trifluoromethyl)-3,3-difluorocyclopropene (17), when reacted with cyclopentadiene, to imitate the propensity of other cyclopropenes towards preferential, if not exclusive, endo addition.[15,18,19,20] However, Sargeant proposed the exo compound 28 as the major reaction product. Also, cyclopentadiene adducts of this general type are believed as a rule to be more thermodynamically stable when in the exo form,[1,45] in spite of any steric interaction

between a syn bridge hydrogen and a cyclopropyl methylene substituent. Thus, the isomerization of 28 to 27 envisaged by Sargeant would not be anticipated based on the relative thermodynamic stabilities of the two isomers. In addition, the assertion by Sargeant that exo 28 isomerizes to endo 27, which further rearranges to the tetracyclic system 29 as shown below seems curious in that conversions of the type that give tetracyclic products such as 29 are believed to take place from the exo stereoisomer.



28 27 29

Further examination of the nmr data for 27 and 28 also suggests that their structural assignments are reversed. Recent analysis[46] of the ^{1}H nmr spectrum of endo-1,5,6,7-tetrachlorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (30) has shown



30

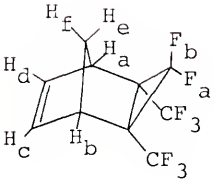
that substantial long range coupling amount to 2.5 Hz exists between the anti bridge proton H_2 and the outside cyclopropyl

methylene proton H_4. Since $^1H - ^{19}F$ long range couplings are usually larger in magnitude than the corresponding $^1H - ^1H$ couplings,[47] the ^1H and ^{19}F spectra of the adduct thought by Sargeant to be endo (27) should contain evidence of long range $^{19}F - ^1H$ coupling from anti proton H_f to the outside fluorine F_a. According to the assignments made by Sargeant, though, F_a appears as a clean septet coupled only to the CF_3 groups (J = 19.0 Hz). There is also an unassigned coupling to F_b of 2.8 Hz. However, in 30, $J_{1,4}$ is only 0.30 Hz, so that the coupling F_bH_e could possibly be 2.8 Hz, but no data pertinent to this question are available at the present time.

Turning to 28, claimed to be exo by Sargeant, there is a large coupling to F_a (cis to the CF_3 groups), amounting to 8.5 Hz, which Sargeant left unassigned. Noteworthy also is that of the two bridge protons H_e and H_f, only H_f, at δ1.84, has a $W_{1/2}$ (~7 Hz) sufficient to possibly accommodate an 8.5 Hz long range fluorine coupling. In view of the contradictions manifested by 27 and 28 in their chemical behavior as well as the anomalies present in their nmr spectra, it is instructive to reverse their stereochemical assignments. That is, assuming 27 to be exo (27a) and 28 to be endo (28a), it is possible to analyze and assign the observed nmr data more satisfactorily. The revised exo/endo assignments are presented in Table V with the appropriate nmr data. Examination of the revised assignments in Table V leads to a more satisfying fit with empirically determined

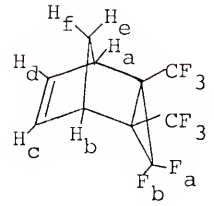
Table V

^{1}H and ^{19}F nmr Data for 27a and 28a



27a

	δppm	mult.	splittings, Hz	assign.	J,Hz
	δH				H_eH_f=8.6
	6.72	1	$W_{1/2}$ ~ 5.5	c,d	F_aCF_3=19.0
	3.57	1	$W_{1/2}$ ~ 6.5	a,b	F_bCF_3=2.6
	2.01	1	$W_{1/2}$ ~ 4	f	F_aF_b=178
	1.15	1	$W_{1/2}$ ~ 8	e	$F_bH_?$=2.8
	δF				
	59.9	2 X 2	19.0, 2.6	CF_3	
	113.7	7	19.0	F_a	
	129.9	2 X 7	2.8, 2.6	F_b	



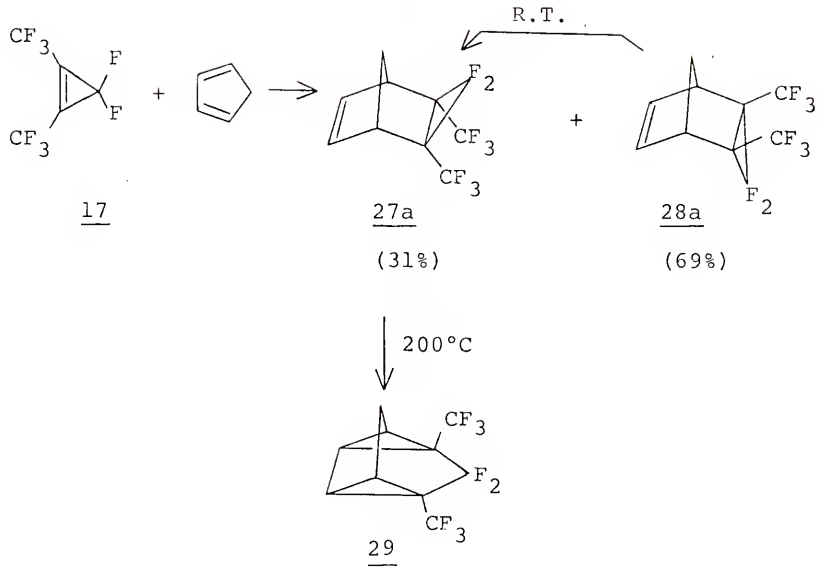
28a

	δH				H_eH_f=8.4
	6.27	2 X 3	3.0	c,d	F_aCF_3=19.0
	3.57	1	$W_{1/2}$ ~ 6.5	a,b	F_bCF_3=2.6
	2.36	1	$W_{1/2}$ ~ 5	e	F_aF_b=177
	184	1	$W_{1/2}$ ~ 7	f	F_aH_f=8.5
	δF				
	61.7	2 X 2	19.0, 2.6	CF_3	
	109.4	7 X 2	19.0, 8.5	F_a	
	136.0	7	2.6	F_b	

trends in the nmr spectra of tricyclic compounds of this type. First, the appearance of H_e at higher field than H_f is consistent with shielding of H_e by the exo cyclopropane ring. Note that δH_e in endo 28a is greater than δH_e in 27a, supporting this mode of shielding for the exo compound. Second, a tentative assignment of $J_{F_b H_{a,b}}$ in 27a can be made, since 4-bond ^{19}F - ^{1}H coupling of the order of 2.8 Hz is not unusual.[35,47] Lastly, the most telling argument for the structural assignments above is the assignment of the large (8.5 Hz) long range ^{19}F - ^{1}H coupling of F_a to H_f, which in 28a should be much larger than any long range ^{19}F - ^{1}H coupling in 27a.

If 27a and 28a are indeed the correct structures for Sargeant's adducts, the isomerization data he reported adhere more closely to the known thermal behavior observed in other exo and endo tricyclic compounds.[1,48] In addition to the fact that the preferred endo adduct 28a now becomes the major reaction product, the isomerization at room temperature of the less stable 28a to the more stable exo isomer (27a) now parallels existing data.[1,48] Also, the quadricyclic product 29 as depicted below is now seen as arising from 27a upon heating at 200° C instead of from 28a, again in conjuction with previous data.[18,23,48]

To conclude, then, that 27a and 28a are the correct structures for the Diels-Alder adducts synthesized by Sargeant seems quite reasonable, in terms of both their chemical behavior as well as the nmr spectral data reported.



17 27a (31%) 28a (69%) 29

Recent work by Jefford et al.[49] involving difluorocarbene addition reactions (which will be discussed later) has, in fact, given strong indications that our reassessments of the structures of 27 and 28 and their spectra are most probably correct.

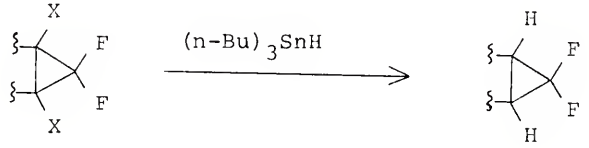
Unfortunately, there are several inconsistencies in the data reported[31] for the cyclopentadiene adduct 26 of perfluorocyclopropene (16), which make the unambiguous assignment of stereochemistry impossible. For example, F_a appears at higher field than F_b, in contrast to previously reported[35] data for other gem-difluorocyclopropene adducts. Also, a coupling of 2.3 Hz is assigned to $J_{F_cH_{a,b}}$, whereas this type of coupling should probably be on the order of 3.5 - 4.0 Hz.[20, 21, 42, 43]

Objectives of This Work

Given the number of Diels-Alder adducts of perhalocyclopropenes that have been prepared and the paucity of definitive structural information about these compounds, there was an obvious need for reinvestigation of many of the reactions in question with an eye towards establishing reliable criteria for making structural assignments in these systems, as well as correcting any erroneous structural assignments. To develop the synthetic potential[50] of cyclopropene Diels-Alder reactions to the utmost, those who utilize these cycloadditions must have at their disposal the means by which exo/endo assignments can be made with certainty. Several methods by which such assignments may be made lend themselves to the work in question. The most likely methods to be used are the spectroscopic techniques, especially ^{19}F and ^{1}H nmr. But for these to acquire the reliability sought, a great many more data must be compiled for a variety of structural types. However, the method that is possibly the most unassailable, and a technique which is coming more and more into prominence in organic structural studies, is single crystal X-ray analysis. This method has the advantage of requiring a minimal amount of material, and since the output is usually in the form of computer drawn structures, relatively subtle differences in bonding or stereochemistry, which might be undetectable otherwise, can be clearly ascertained.

Our objective was to establish the structure of one of

the previously reported fluorinated cyclopropene adducts by X-ray crystallography, and then using the ^{1}H and ^{19}F nmr parameters for this "known" system, to develop nmr spectral criteria for making structural assignments in related systems. Included in this endeavor was the synthesis not only of the cyclopropenes and the Diels-Alder adducts thereof, but chemical conversions of most of these adducts to new compounds so that the methodology used might be expanded to include more structural types. Specifically, these transformations consisted of reducing the C=C double bonds in some adducts and/or treatment of these vic-dihalo-gem-difluorocyclopropanes with tri-n-butyltin hydride to obtain the corresponding gem-difluorocyclopropanes. The characterization of these compounds was expedited by the distinctive ^{1}H and ^{19}F nmr spectra of the general structure shown below.



X = Cl, Br

It is interesting to note that the synthetic step depicted above is equivalent with respect to the overall structures involved to (i) performing the original Diels-Alder reaction using 3,3-difluorocyclopropene as the dienophile, or (ii) addition of the difluorocarbene ($:CF_2$) moiety

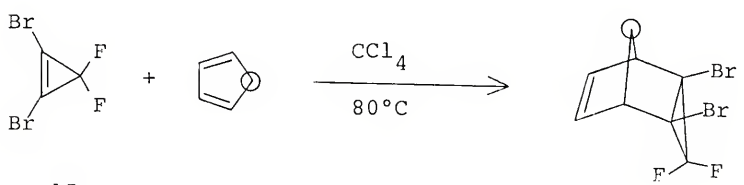
to a cyclic or bicyclic olefin. What may not be as analogous is the stereochemistry of the products so obtained. For example, while some of the [4 + 2] cycloadditions might yield endo products, their exo analogs should be obtainable via the difluorocarbene sequence. The discussion of the details of our synthetic investigations of 3,3-difluorocyclopropene as well as discussion of difluorocarbene additions will be deferred until the appropriate time in Chapter II, in order to avoid redundancy.

CHAPTER II

RESULTS AND DISCUSSION

Stereochemical Studies of Perhalocyclopropene [4 + 2] Cycloadducts

As discussed earlier, in light of the imprecise nature of assigning stereochemistry to Diels-Alder adducts of perhalocyclopropenes, it was our belief that a means should be found to unambiguously assign an exo or endo structure to one such compound, and then apply the spectral parameters observed for that compound to other similar adducts of unproven structure. We selected as our model system 2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (20), first prepared by Law and Tobey in 1968[35] from 1,2-dibromo-3,3-difluorocyclopropene (15) and furan, and assigned the endo structure shown. This compound is one of the "stable"



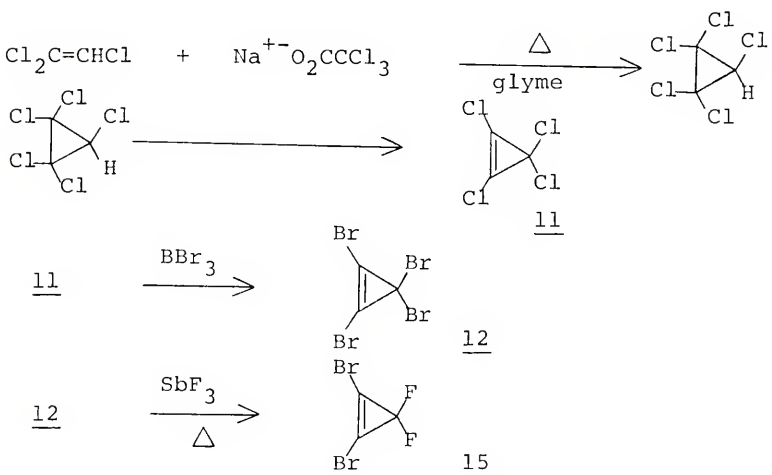
15 20

adducts of this general type that have been prepared, meaning that 20 appears to be thermally stable to ring opening

reactions at 100° C, the pot temperature used by Law and Tobey in their distillation of 20. As elaborated earlier, nmr spectroscopy did not provide a suitable proof for the stereochemistry of 20. To this end, it was deemed essential that a single crystal X-ray analysis should be carried out on the same material that was reported by Law and Tobey.

Synthesis of 20 naturally required 15 as a precursor, and the reaction sequence developed by Tobey and West[26,27,28] was repeated, as shown in Scheme I (for specifics concerning yields, etc., see Experimental). The Diels-Alder reaction

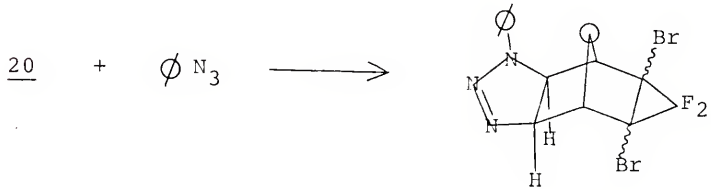
Scheme I



was carried out as described by Law and Tobey. Instead of using only a short path distillation, however, our crude reaction mixture was passed through florex with pentane,

the solvent was removed, and the residue was sublimed to give a material which had all spectral properties identical to the literature report.[35] Oddly, the melting point of the sublimed adduct was 36° lower than the literature value, so that the state of purity of the material from our sublimation required closer examination. Analysis by gas chromatography as well as reexamination of the ^{19}F nmr spectrum of this material indicated that only one adduct was present, and that it was indeed identical to the compound reported as 20.

Having established the authenticity of our furan adduct, the next step in the structural determination was the reaction of 20 (20a) with phenyl azide (31) to form a 1:1 adduct, 32. There were two major reasons for preparing 32.



32

First, 20 (20a) proved to be far too volatile at room temperature to permit analysis by X-ray diffraction, and second, although 20 (20a) was a solid, 32 formed crystals that were more amenable to the shaping and mounting procedures required for single crystal X-ray studies (see Experimental). The results of the X-ray structural determination are shown in

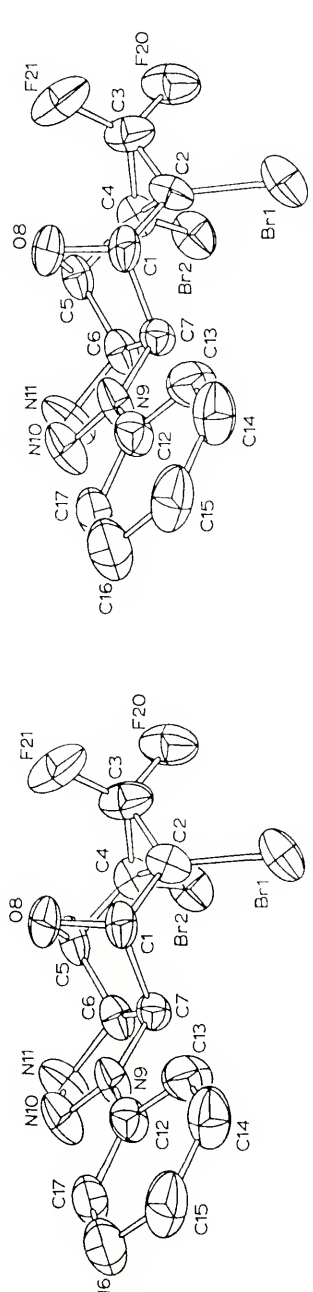
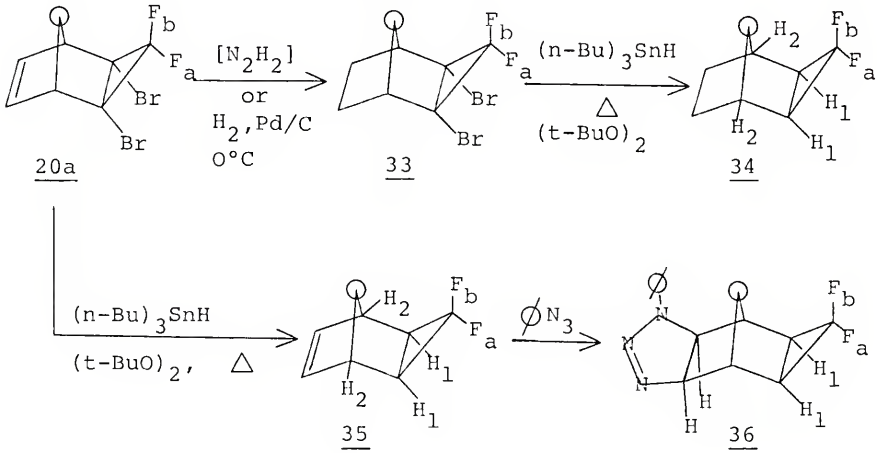


Figure 1. Stereoview of Phenyl Azide Adduct 32

Figure 1, which is a stereoview of the complete structure of 32. As anticipated,[51] the phenyl azide moiety added to 20 (20a) in a 1,3-dipolar fashion, resulting in the formation of the exo 5-membered ring. Of paramount importance, however, as Figure 1 unmistakably shows, the gem-difluorocyclopropane ring also has the exo stereochemistry. One consequence of this finding is that the structure of the original Diels-Alder adduct (from which 32 was synthesized) had to be 20a, the exo structure discussed earlier, and not 20, the endo isomer originally proposed by Law and Tobey. The immediate impact of this single result was that the stereochemistries assigned to the other furan adducts prepared by Law and Tobey[35] as well as those prepared by Sargeant,[31] required reevaluation.

Using 20a, now known to be exo, as starting material, three other compounds were synthesized from it that retained the gem-difluorocyclopropane ring. These chemical transformations are shown in Scheme II. It should be noted that

Scheme II



of the reactions used in Scheme II, none are currently suspected of causing exo to endo isomerizations, either by a retro-Diels-Alder type mechanism, or by inversions at individual carbon centers. In support of our contention that all of the compounds in Scheme II have the exo structures shown, is the ^{19}F chemical shift of F_b, which for the brominated compounds 20a and 33 has values of 136.5 ppm and 135.5 ppm, respectively (also, as further proof, in the phenyl azide adduct 32, δF_b is 134.2 ppm), indicating that F_b in each case resides in approximately the same environment. When the bridgehead Br atoms are reduced to hydrogen atoms, as in 34, 35, and 36, F_b now appears at 145.9 ppm, 143.4 ppm, and 144.9 ppm, respectively, again indicative of equivalent environments in these compounds, as well (for complete ^1H and ^{19}F nmr data, see Table IX, p 87). Of course, correct assignments of F_a and F_b are crucial if the observed trends in ^{19}F nmr chemical shift values are to be of any use. In 34, 35, and 36 (and hence in their precursors in Scheme II) this task is made trivial by observation in the ^{19}F spectra of the large (12-13 Hz) triplet coupling of F_a to the cyclopropyl protons. This cis-vicinal ^{19}F - ^1H coupling is much larger than the trans-vicinal ^{19}F - ^1H coupling, which is 1.5 - 2.5 Hz. Therefore, in principle, if a gem-difluoro-1,2-dihalocyclopropane can be successfully reduced in the manner shown above, ^{19}F nmr assignments should be rather straightforward.

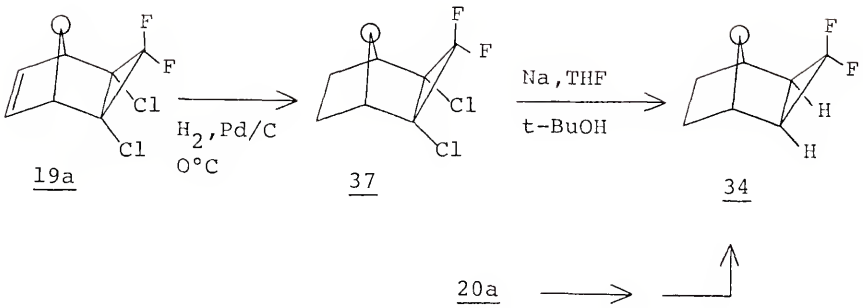
In conjunction with the above technique, correct assignment of stereochemistry in analagous compounds can now be

made by conversion of one of the compounds of known stereochemistry to a compound which can also be derived from an adduct of unknown structure. In lieu of this direct method, since such conversions are not always possible, we have made use of three other spectroscopic techniques for determination of stereochemistry. The first of these techniques involves measurements in ^1H nmr spectra of line widths at half height ($W_{1/2}$), which gives a measure of the maximum value that can be attributed to all couplings to the particular nucleus under scrutiny. For example, in the ^1H nmr spectrum of 35, $W_{1/2}$ for the cyclopropyl protons (H_1) is 0.75 Hz, indicating that $J_{H_1H_2}$ must be no greater than this ceiling value. If 35 were endo, $J_{H_1H_2}$, and hence $W_{1/2}$ for H_1 would be expected to be much larger, as discussed previously.[41,42] Measurements of $W_{1/2}$ will henceforth be quoted when they are relevant to structural assignments. Secondly, and as a further refinement of the $W_{1/2}$ technique, we employed heteronuclear decoupling to provide another means of estimating coupling constants such as $J_{H_1H_2}$. In a typical experiment, each ^{19}F nucleus was irradiated in turn and the resulting ^1H nmr spectrum was recorded. Also, due to the $\Delta\delta$ between ^1H and ^{19}F nuclei, both F_a and F_b could be simultaneously irradiated, giving a fully decoupled ^1H nmr spectrum. This method, therefore, provided a way of obtaining $W_{1/2}$ data from ^{19}F decoupled spectra, which, when considered with the undecoupled spectra, usually allowed for more certain exo/endo assignments. Heteronuclear decoupling proved to be quite

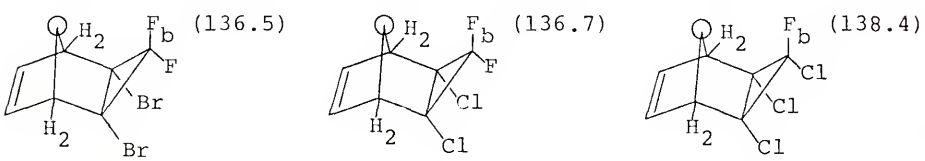
useful for furan adduct assignments as well as for adducts of some cyclopentadienes, which will be discussed later. Finally, in those cases where an oxygen atom formed a bridge in an adduct (of furan and related dienes), we had hoped that the use of $Eu(FOD)_3$ as a shift reagent might give rise to a correlation between stereochemistry and the observed rate of shift for the ^1H resonances. The results we obtained using 34 as a reference compound will be discussed at the appropriate time, and although they were not as quantitative as we had hoped, some interesting trends were observed from which tentative inferences regarding the nature of $Eu(FOD)_3$ complexation can be drawn.

Since 20a, as prepared by Tobey and Law,[35] had the exo structure as shown by X-ray analysis, the prospect of detecting additional incorrect assignments became much more likely. These suspicions were well founded, since the furan adduct (19) of 1,2-dichloro-3,3-difluorocyclopropene (14), considered to be the endo isomer by Tobey and Law, also proved to have exo stereochemistry. Our proof of structure consisted of duplicating the original synthesis of "19", followed by saturation of the double bond to give 37 and reduction of the methine Cl atoms, as shown in Scheme III. The resulting saturated, dechlorinated material had an infrared spectrum identical to the infrared spectrum previously recorded for 34, prepared from authentic exo 20a. In retrospect, since the chemical shifts of F_b in 20a, 19a, and the lone ^{19}F in 18 (see Table I) fall within 2.0 ppm of

Scheme III



each other, the preliminary conclusion that all three of these fluorocyclopropene adducts are exo has now been firmly established for 20a and 19a, and a strong case can now be made for exo stereochemistry of the monofluorocompound 18 (as 18a) as well. Noteworthy also, is the similarity of



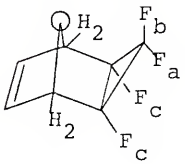
$J_{F_bH_2}$=2 $J_{F_bH_2}$=2.5 $J_{F_bH_2}$=2.5

20a 19a 18a

$J_{F_bH_2}$ in all three compounds, which also points up the resemblance in the structural environments for F_b in 18a, 19a, and 20a.

Bearing in mind the values for δF_b cited above, the previous discussion of the furan adducts 21 and 22, reported by Sargeant[31] to be endo, becomes more germane. If these

compounds are now taken to be exo, as mentioned previously, the correlation between δF_b, $J_{F_bH_2}$, and exo stereochemistry can be extended to 22a. The case of 21a has not yet been



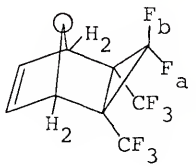
(139.3)

$J_{F_aH_2}$=3.2?

$J_{F_bH_2}$= ?

$J_{F_cH_2}$= ?

21a



(137.0)

$J_{F_bH_2}$=1.2

22a

resolved, since Sargeant quoted no values for $J_{F_bH_2}$ or $J_{F_cH_2}$ and there is still his reported $J_{F_aH_2}$ = 3.2 Hz to be considered in terms of making a satisfactory structural assignment. Thus, no definite choice between endo 21 and exo 21a can be made at this point.

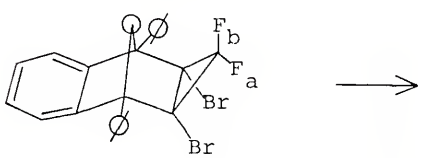
Thus, having made the necessary corrections to the structures erroneously designated as endo [4 + 2] adducts of furan and some fluorinated cyclopropenes, attention was turned to the synthesis of new perhalocyclopropene-furan adducts, and then using the criteria discussed in relation to 20a, to extend the number of unambiguous structural assignments in this system. For several reasons, 1,2-bromo-3,3-difluorocyclopropene (15) was the dienophile of choice, even though its preparation involved four steps (see Scheme I) with an average overall yield of about 3%. First, 15 was used in the initial work in the X-ray analysis, and to change the nature of the dienophile in use would have added another

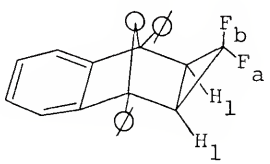
variable to a mechanistic scheme already laced with uncertainties. Second, from a more practical standpoint, of the gem-difluorocyclopropenes previously discussed, 15 had the advantages of being thermally stable, non-volatile, and most important, of possessing moderate relative reactivity towards dienes.[35] A choice of some other gem-difluorocyclopropene would have meant compromising some or all of the advantages of 15.

The first diene we chose to react with 15 was 1,3-diphenylisobenzofuran, which is also thermally stable yet fairly reactive towards dienophiles, due to the incipient aromaticity of the benzo- moiety in the transition state for adduction. When this reaction was carried out at 80° C for 12 hours, the product consisted of 89.9% exo-2,4-dibromo-3,3-difluoro-1,5-diphenyl-[6,7]benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (38a) contaminated with 10.1% of the endo isomer 38. These assignments can be advanced on the basis of the X-ray study done by Bordner and Howard[38] which proved that tetrachlorocyclopropene (11) also gives an exo adduct with 1,3-diphenylisobenzofuran. Also, on chemical grounds, the product predicted to be the most stable isomer would be exo (38a), and thus at 80° C should also be the major product. The evidence to support the endo structure 38 consists of the lack of signals in the ^{1}H and ^{19}F nmr spectra which could correspond to another type of structural isomer. That 38 is a structural isomer of 38a was borne out by the fact that the mixture gave a correct elemental analysis for the formula of

38a/38. Also, the ^{19}F nmr spectrum of 38 was completely analagous to that of 38a, consisting of a doublet of doublets with $J_{F_aF_b}$ = 144.0 Hz. The intriguing question of exo/endo isomerism will be discussed later in relation to the 20/20a system, which was studied more extensively.

Also, when 38a (+38) was treated with tri-n-butyltin hydride at 100° C, only one product was formed, and was assigned the exo structure 39 shown below. The ^{19}F nmr





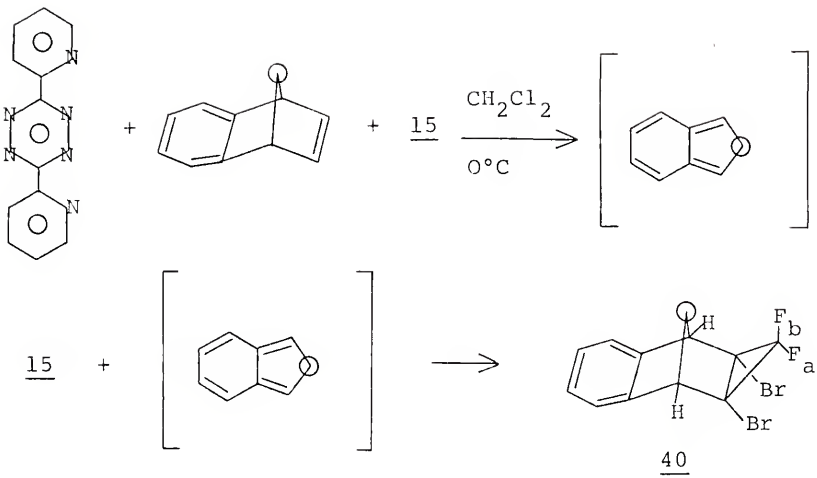
	38a	[20a]		39	[35]
F_a	93.3	[92.6]	F_a	108.7	[105.0]
F_b	129.5	[136.2]	F_b	142.6	[143.4]

chemical shift data for 38a and 39, as compared to the analagous data for 20a and 35 (from the furan series, see Scheme II), shown in brackets above, speak favorably for both 38a and 39 to be exo. Law and Tobey[35] observed considerable internal consistency in their data, and used this as an argument for like stereochemistries in their compounds. Even though their assignments appear to be reversed, the trends in the data are still useful. Similarity of ^{19}F nmr chemical shifts can be quite valuable in settling questions of stereochemistry, but in order to be of any value, the

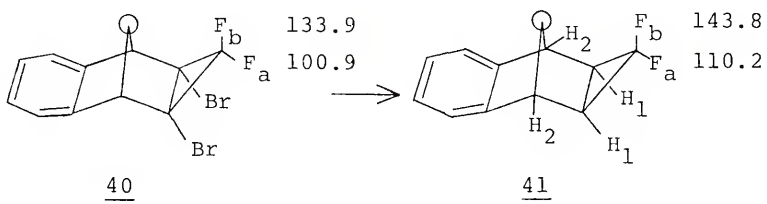
individual ^{19}F resonances must be assigned to the proper ^{19}F atoms in the proposed structure. Therein lies another advantage of converting the methine cyclopropyl Br atoms in adducts such as 20a or 38a to hydrogen atoms as in their reduced counterparts 35 and 39. Assignment of the ^{19}F cis-vicinal coupling constant to these protons is simply a matter of finding the ^{19}F resonance with a large (10 - 15 Hz) J_{FH} cis-vic. The ^{19}F trans-vicinal coupling is small (1 - 2 Hz) but also measurable in the ^{19}F nmr spectrum. This general method of confirming ^{19}F nmr assignments was used throughout this work, and as a result, the ^{19}F nmr assignments in Table IX should be accurate.

If the phenyl groups in 39 were replaced by hydrogens the resulting compound would provide an opportunity for measuring coupling between the bridgehead protons and the methine cyclopropyl protons, which would be useful in making stereochemical assignments. This system would have a simple ^{1}H nmr spectrum, showing only three well separated signals, and thus would also lend itself to facile $W_{1/2}$ measurements in both the normal spectrum and the ^{19}F decoupled spectrum. Of course, this hypothetical system corresponds to the [4 + 2] cycloadduct of 15 with the parent isobenzofuran. The method of choice for generating isobenzofuran in situ and the one that we employed in our reaction with 15 was that of Warrener,[52] as shown in Scheme IV. The [4 + 2] adduct 40 was immediately suspected of being exo on the basis of the ^{19}F nmr chemical shifts when they were compared to other "known" compounds, as

Scheme IV



discussed previously. Once again, reduction of 40 to 41 with tri-n-butyltin hydride allowed confirmation of the ^{19}F nmr assignments and thus lent support to the exo



structures shown for 40 and 41.

Additional evidence for structure 41 was obtained from its ^1H nmr spectrum, which consisted of an aromatic AA'BB' multiplet, a doublet for the bridgehead protons (H_2), and a doublet of doublets for the methine cyclopropyl protons (H_1). Since the signals for H_2 and H_1 were widely separated,

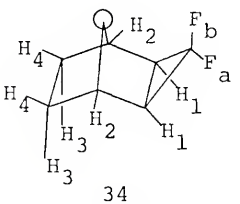
$W_{1/2}$ for them was easily obtained. In the undecoupled spectrum of 41 $W_{1/2}$ for each half of the H_2 doublet was 1.0 Hz, in agreement with the expected small value for $J_{H_1H_2}$ if 41 were exo. When F_b was irradiated, the H_2 doublet collapsed to a sharp singlet, and the doublet of doublets for H_1 became a doublet, retaining only the larger cis-vic coupling ($J_{F_aH_1}$). Conversely, when F_a was irradiated, the H_2 doublet was unchanged, and the remaining doublet for H_1 showed only the small trans-vic $J_{F_bH_2}$. This experiment demonstrated the utility of heteronuclear decoupling in confirming ^{19}F nmr assignments as well as determining the extent and nature of long range ^{19}F - ^{1}H couplings, and by performing such an experiment on 41, we confirmed that our $W_{1/2}$ measurement of 1.0 Hz for $J_{H_1H_2}$ was a maximum value.

The use of nmr shift reagents with compounds in the general class we were studying seemed to be appropriate, since, as a rule, the rate of shift of a given ^{1}H resonance is inversely proportional to the distance between the lanthanide metal atom and the proton in question. In compounds such as 41, with two possible stereoisomers, it was hoped that the rates of shift for exo vs endo protons could be correlated, once the corresponding rates for a compound of known stereochemistry had been ascertained. As our reference compound, 34 was used since it had the prerequisite oxygen bridge (for a $Eu(FOD)_3$ metal coordination site) as well as protons on the cyclopropane ring that were known to

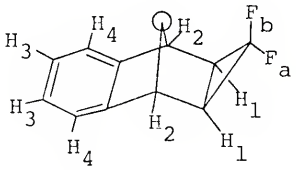
be endo (for details of the method, see Experimental). A comparison of the rates of shift (k) for protons in 34 and 41 is given in Table II. The overall trends in the

Table VI

Comparison of $Eu(FOD)_3$ nmr shift results for 34 and 41



34



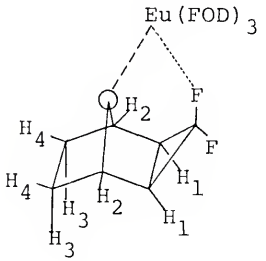
41

	k_{avg}		k_{avg}
H_1	0.774	H_1	0.436
H_2	1.74	H_2	3.97
H_3	0.603	H_3	0.00
H_4	0.645	H_4	0.0064

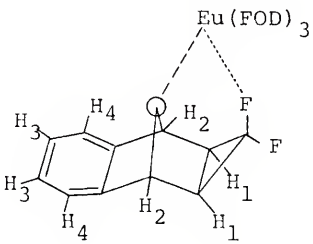
data of Table II are in agreement for exo structures 34 and 41, in that the signal for H_2 in both compounds exhibits the highest rate of shift. Also, k_{H_1} for 34 and for 41 is much smaller than k_{H_2}, but if the k_{H_2}/k_{H_1} ratio is calculated, it has values of 2.25 for 34 and 9.11 for 41. In quantitative comparisons of this type, a closer correlation would be desirable and necessary if the method is to be more generally applicable.

The discrepancy in k_{H_2}/k_{H_1} for 34 and 41 is most probably

due to a difference in the geometry of complexation of $Eu(FOD)_3$ by the two compounds. It is known that $Eu(FOD)_3$ will weakly coordinate to ^{19}F (and produce contact shifts in the ^{19}F nmr spectrum),[53] so that weak secondary coordination with ^{19}F in 34 and 41, as shown below, might cause a slight off-centering of the Eu atom with respect to the



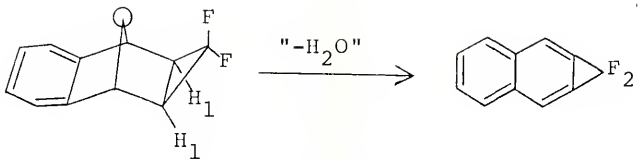
34



41

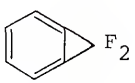
oxygen bridge, with the Eu atom residing more of the time syn to the cyclopropane ring. If this is the case, the similarity of k_{H_3} and k_{H_4} in 34 comes as no surprise, nor do the negligible values for k_{H_3} and k_{H_4} in 41 seem unusual. Speculations of this type may provide satisfying explanations in individual cases such as the ones above, but these same rationalizations undermine the generality of the method.

However, the other evidence obtained from $W_{1/2}$ measurements and heteronuclear decoupling experiments plus the chemical analogy between 40, 41, and similar compounds known to be exo leaves little doubt that 40 is the exo adduct of 15 and isobenzofuran. As an interesting sidelight, 41 can also be recognized as a precursor to 1,1-difluoronaphthocyclopropene (42), with the proposed conversion formally



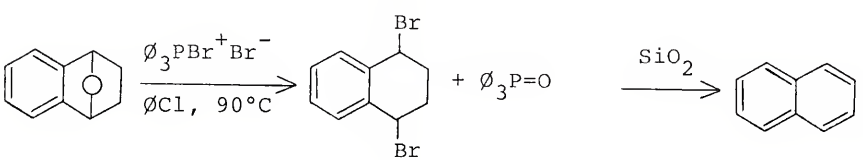
41 42

considered as an overall loss of water from 41. Vogel et al.,[54] had previously prepared 1,1-difluorobenzocyclopropene (43), so that 42 would be an interesting extension



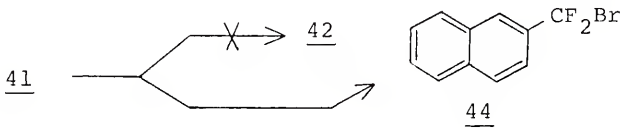
43

of these authors' investigation into the question of bond fixation in benzo-annelated cyclopropenes. The actual conversion of 41 to 42 was thought possible in light of recent work[55] in which 1,2,3,4-tetrahydronaphthalene-1,4-endoxide was converted to naphthalene with triphenylphosphine dibromide via an intermediate dibromo compound, as shown below. Under the conditions of the reaction of 41 with



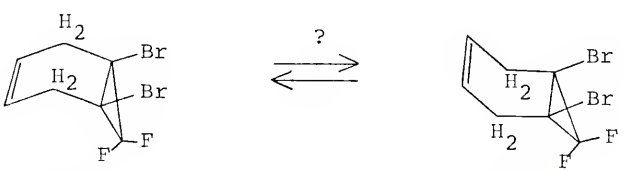
triphenylphosphine dibromide and subsequent silica gel

chromatography, the oxygen bridge was indeed cleaved, but with concomitant ring opening, so that the only isolated product derived from 41 was not 42, but β-bromodifluoromethyl)naphthalene (44). That the gem-difluorocyclopropane



ring was opened (apparently by Br^-) under prolonged heating was not too surprising due to the probable susceptibility of the gem-difluoro carbon atom to nucleophilic attack.

Turning to reactions of 15 with acyclic dienes, Law and Tobey[35] had prepared the adduct 45 of 15 with 1,3-butadiene, which was converted to 1,1-difluorobenzocyclopropene by Vogel and coworkers.[54] Due to the lack of substituents on the butadiene moiety in 45, the stereochemistry of addition is irrelevant, but there still exists the possibility of conformational isomerism. Law and Tobey[35] represented 45 as 45b only, based on the ^{19}F couplings to

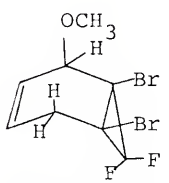


45a 45b

the methylene protons (see Table IX). According to these

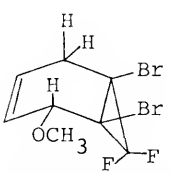
authors, 45b has fewer steric interactions than 45a and is thus the preferred conformation. Of relevance to our work is their comment that the $J_{^{19}F-^{1}H}$ data seem to indicate that 45 exists in a "flip form opposite..." to the conformation of this structure if an oxo- bridge were present. That is, the bicyclic moiety in 45 appeared to them to be opposite in structure to this same group in the furan adduct of 15. However, since the furan adduct (20a) is in fact exo, their analysis would lead to a prediction of the less stable conformer 45a as the species most consistent with the nmr data.

In order to resolve this question of stereochemistry, if possible, and to investigate a cycloaddition of 15 to an acyclic, unsymmetric 1,3-butadiene for comparison to the furan series, we elected to use 1-methoxy-1,3-butadiene in a reaction with 15. The presence of the methoxy substituent introduces the possibility of stereoisomerism in the adduct 46, in addition to the previously existing possibility of conformational isomerism in each stereoisomer. The resulting four possible structures for 46(a-d) are shown below, and are classified as exo or endo with respect to the



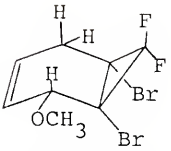
exo methoxy

46a



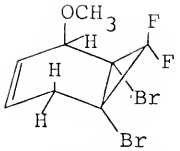
endo methoxy

46c



exo methoxy

46b



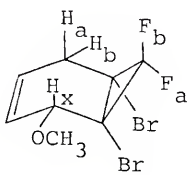
endo methoxy

46d

46a ⇌ 46b

46c ⇌ 46d

placement of the methoxy group. Due to steric repulsions, the folded forms 46a and 46c would be expected to be less stable than 46b and 46d. Therefore the choice of which isomer was actually produced in the reaction was narrowed to one of the latter two structures. The ^{19}F nmr spectrum made it possible to assign 46b as the correct structure, since F_a (at lowest field) appeared as a doublet of triplets ($J_{F_aF_b}$ = 155 Hz, $J_{F_aH_a}$ = $J_{F_aH_x}$ = 3.2 Hz) and F_b appeared as a doublet of doublets ($J_{F_bH_b}$ = 2.4 Hz), as shown below with the observed ^{19}F chemical shifts. The analogy between $J_{F_bH_b}$

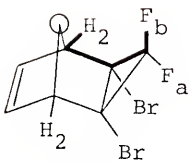


138.51 (d of d)

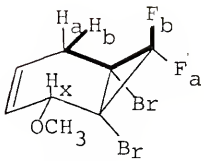
113.92 (d of t)

46b

in 46b (2.4 Hz) and $F_{F_bH_2}$ in 20a (2.1 Hz), shown by the darkened lines below, and the larger value for the triplet coupling $J_{F_aH_{x,a}}$ (3.2 Hz), which was not possible in 20a,

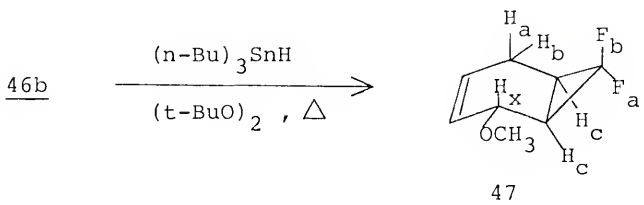


20a



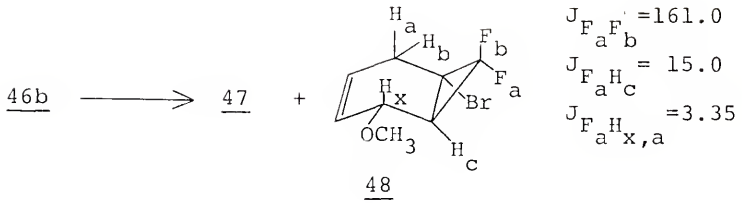
46b

of course, argued for structure 46b. The ^{19}F nmr assignments in 46b were confirmed by reduction of the methine cyclopropyl bromines with tri-n-butyltin hydride, which produced the dihydro compound 47 which had the characteristic triplet for F_a in the ^{19}F nmr with cis-vic coupling $J_{F_aH_c}$ of 14.0 Hz. Unfortunately, the remainder of the ^{19}F



47

nmr spectrum, as well as the ^{1}H nmr spectrum, proved to be too complex to allow further evaluation of other coupling constants. Interestingly, a minor artifact of the reduction was a monobromo product, which could be identified as 48 using ^{1}H nmr chemical shifts and ^{19}F-^{1}H coupling constants. The chemical shift of H_x (δ4.16) in 48 was quite close to that of H_x in 47 (δ3.91). However, $H_{a,b}$ in 48 appeared at δ2.87, shifted downfield more than 0.5 ppm by the vicinal cyclopropyl bromine atom, relative to $H_{a,b}$ in 47, which

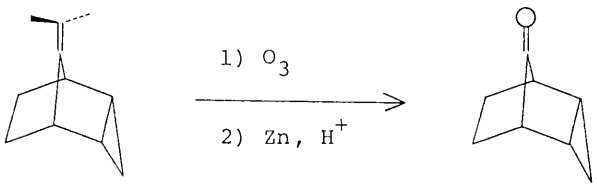


48

appeared at δ2.33. Also, F_a in the ^{19}F nmr spectrum of 48 appeared as a doublet ($J_{F_aF_b}$ = 161.0 Hz) of doublets ($J_{F_aH_c}$ = 15.0 Hz) of triplets ($J_{F_aH_{x,a}}$ = 3.35 Hz), and was the ^{19}F at lowest field (δ97.74). The monobromo product which best fits these data is 48. Therefore, the results obtained for the reaction of 15 with 1-methoxy-1,3-butadiene correspond to an exo cycloaddition, assuming that 1-methoxy-1,3-butadiene is trans. Also, this reaction demonstrates that information regarding stereochemistry of [4 + 2] additions of perhalocyclopropenes to acyclic 1,3-dienes can be obtained if the diene has a nonsymmetric substitution pattern. Correct deduction of the product structure will give an indication of relative conformational stabilities and may provide clues as to the structure of the transition state leading to the observed product. But quantitative evaluation of all of the steric and electronic factors in a [4 + 2] cycloaddition reaction such as the one above is a complex undertaking, so that care must be taken not to attribute total control of the transition state geometry to any single factor, excluding other subtler influences

which may be the real controlling factors.

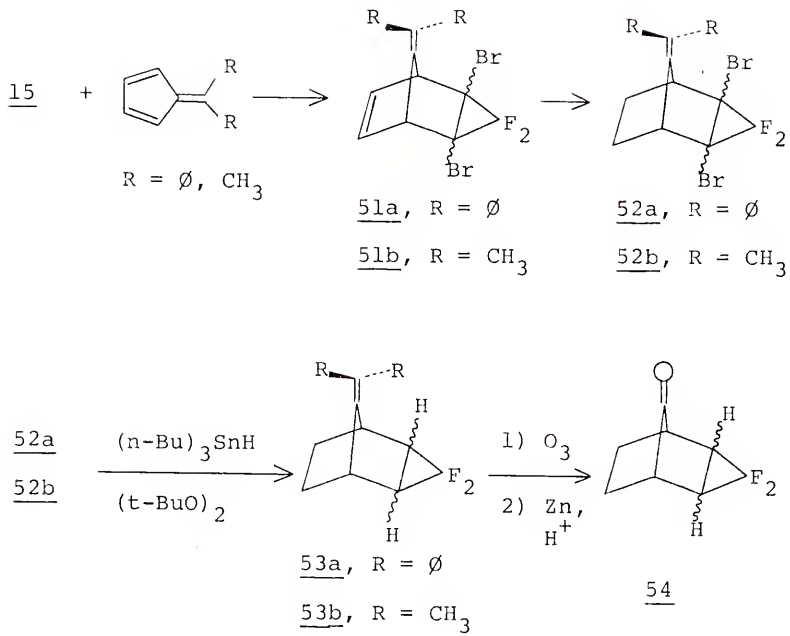
As outlined in the Introduction, alkyl- and aryl-cyclopropenes have been known to react with fulvenes in a [4 + 2] manner,[17,18] and the resulting adducts can be further modified to give materials that are useful in structure-reactivity studies such as solvolysis of alcohol derivatives and ketone decarbonylation. Specifically, Tanida,[17] using a 6,6-dimethylfulvene and cyclopropene, synthesized endo-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (50) by way of oxonolysis of the 8-(dimethylmethylene) compound 49.



49 50

Since we had previously demonstrated that the methine cyclopropyl bromines in some of the furan adducts we had prepared could be reduced with tri-n-butyltin hydride, the application of the technique could be used in the synthesis of a 3,3-difluoro derivative of 50, as shown in Scheme V. It should be noted that even though 50, derived from cyclopropene and 6,6-dimethylfulvene, was proven to be endo by Tanida, the assignment of stereochemistry to 51a and 51b must be based on more than analogy to the hydrocarbon system. Also, our reactions to form 51a and 51b were run at 115° C, in contrast

Scheme V



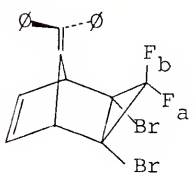
to Tanida's work, which was done at room temperature or lower. This fact combined with the much greater ground state stability of 15 over cyclopropene[35] means that our adducts were formed under conditions that may have been conducive to reversible formation of the more stable exo adducts.

Since adducts 51a and 51b are the first reported products arising from a [4 + 2] reaction of a fulvene with a perhalocyclopropene, stereochemical assignments cannot be based on ^{19}F chemical shifts observed in these compounds without reference data for model systems of known stereochemistry. However, since these adducts were treated with

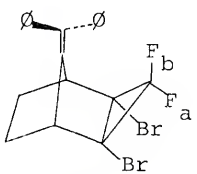
the same reagents as was 20a, and since certain trends in the changes in the ^{19}F nmr spectra of products derived from 20a were noted earlier, some internal comparisons can be made in the sequence 51a,b:52a,b:53a,b. As shown in Table VII, the chemical shifts for F_a in 52a and 52b are virtually identical, as are the analagous values for δF_a in 53a and 53b. This indicates the similarity in the

Table VII

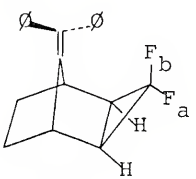
Comparison of ^{19}F Nmr Chemical Shift Data



51a

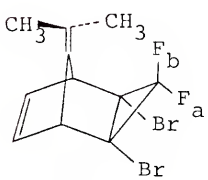


52a

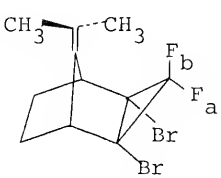


53a

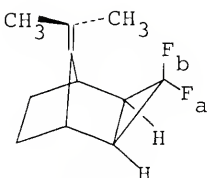
	51a	52a	53a
δF_a	94.48	111.34	124.80
δF_b	131.96	132.65	142.77



51b



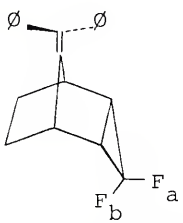
52b



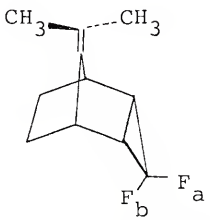
53b

	51b	52b	53b
δF_a	——	110.56	124.14
δF_b	——	136.03	146.75

environments for F_a in each of the pairs of compounds. Turning to the values for δF_b, if both 51a and 51b were endo, the differences in the changes in chemical shift for F_b should also be small, but what was observed proved to be substantial differences in the values for δF_b, when comparisons were made for 52a and 52b, or 53a and 53b. This indicates rather dissimilar environments for F_b in these compounds, whereas the environments for F_a in the same compounds were shown to be quite comparable. If both adducts were endo, the values of δF_a and δF_b ought to be almost identical for 53a and 53b, as shown below, instead



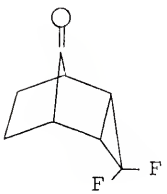
53a (as endo)



53b (as endo)

of exhibiting the differences shown in Table III. Therefore, based on these internal comparisons of ^{19}F chemical shift values, adducts 51a and 51b appear to be exo. The other criteria useful in specifying stereochemistry are not as applicable in these two cases. First, the observance of or the lack of coupling between bridgehead protons and methine cyclopropyl protons in 53a and 53b is obscured by the fact that the bridgehead protons in 52a and 52b, and 53a and 53b, all appear as broad multiplets. All that can be said is that

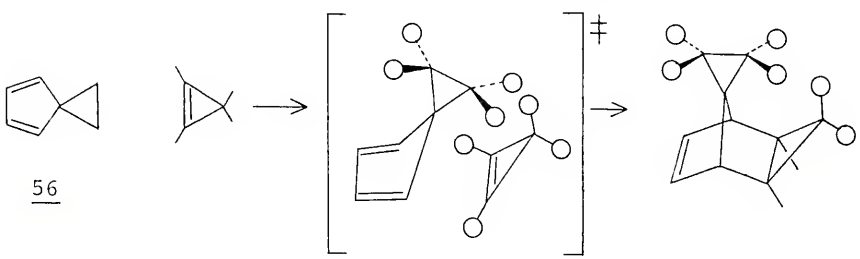
$W_{1/2}$ for 52a and 53a are both 6 Hz, and that $W_{1/2}$ for 52b and 53b are both 5 Hz. While these $W_{1/2}$ values for 53a and 53b could accommodate a coupling of 3-4 Hz for bridgehead proton-methine cyclopropyl proton coupling, the fact that the values do not change upon debromination is supportive of the proposed exo structures. Also, the complexity of the ^1H nmr spectra and the extensive ^1H - ^1H couplings in these compounds renders heteronuclear decoupling almost useless, since the values for $W_{1/2}$ would not change much even if all ^{19}F - ^1H couplings were eliminated. While a $Eu(FOD)_3$ experiment might be of some help in assigning stereochemistry in the ketone 54, it must be mentioned that no $Eu(FOD)_3$ shift data are available for the known epimeric ketones in the non-fluorinated series for comparison, so that this technique is of limited utility. Until such data are amassed, both for model systems (for example, exo- and endo-tricyclo[3.2.1.$0^{2,4}$]octan-8-one) and for ketone 54 (as of this writing, 54 has not yet been characterized), the only indications that both 51a and 51b are exo adducts are chemical intuition (in light of the severe reaction conditions) and more importantly the ^{19}F nmr chemical shift behavior discussed above. If 54 does, indeed, prove to be exo, the synthesis of the epimer, endo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]octan-8-one (55), required for investigations into the effect of fluorine substituents on reactivity in the tricyclo[3.2.1.$0^{2,4}$]-octyl system, becomes much more difficult, since the exo isomer (54) should be obtainable by alternate routes. Also, as will



55

be discussed later, endo 55 may easily isomerize to exo 54 at moderate temperatures.

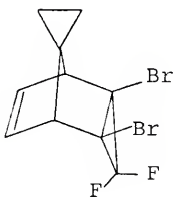
At this time, and taking into consideration the results discussed above for the reactions of 15 with 6,6-diphenyl- and 6,6-dimethylfulvene, the next logical step in our stereochemical studies of the [4 + 2] reactions of 15 seemed to be an attempt to force this cyclopropene into reacting with a diene so as to produce an endo adduct. The diene we chose was spiro 4.2 heptadiene (56), since the spiro methylene groups would appear to place severe steric restrictions on any cyclopropene reacting via the exo mode (see below).



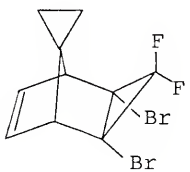
56

Substantial non-bonded interactions should develop between the cyclopropene methylene substituent and the apical cyclopropane hydrogens syn to the reacting cyclopropene molecule. On steric grounds, then, an argument might be made for the

reaction of 56 with 15 to proceed to give an endo adduct. Also, the adduct of cyclopropene with 56 was reported by LaRochelle and Trost[22] to be endo, based on the similarity of its ^{1}H nmr spectrum to other endo adducts of cyclopropene. Conversely, and also on chemical grounds, the exo adduct (57a) of 56 and 15 may well be the more thermodynamically stable isomer, despite the steric interactions mentioned above. The reaction of 56 with 15 was initially



57



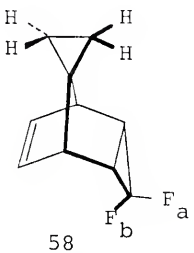
57a

attempted in CCl_4 at 55° C, but the reaction was sluggish at the concentrations used, so that prolonged heating at 55° C proved necessary for complete reaction. Nevertheless, 57 (57a) was isolated, and the spectroscopic and analytical data for it were accumulated, including the ^{19}F nmr chemical shifts. The technique used previously to firmly establish ^{19}F nmr assignments, that is, reduction of the methine cyclopropyl bromines with tri-n-butyltin hydride, was again applied to adduct 57 (57a), to give 58 (58a). At this point, we had firmly established ^{19}F chemical shift data for both the adduct and its debrominated product, as well as ^{1}H nmr data for both compounds. The chemical shift data alone for these two

compounds do not allow for the unambiguous assignment of exo or endo stereochemistry, but comparison of these data to data from the adduct of 15 with cyclopentadiene of known exo stereochemistry leads to the tentative assignment of exo stereochemistry in this case (that is, 57a and 58a).

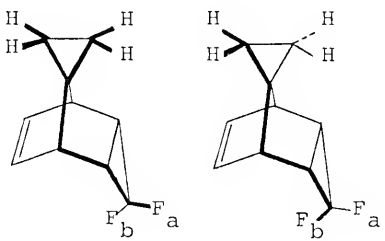
First, measurements of $W_{1/2}$ for the bridgehead protons in 57a and 58a gave values of 7 Hz and 6 Hz, respectively, indicating that any coupling from the methine cyclopropyl protons to the bridgehead protons in 58a is most likely small. Also, in a homonuclear decoupling experiment on 58a, when the bridgehead protons were irradiated, the methine cyclopropyl proton doublet maintained a line width of 3 Hz, which again is contraindicative of significant coupling of the type mentioned above. Second, a heteronuclear decoupling experiment on 58a, in addition to confirming the assignments of F_a and F_b, revealed an interesting six bond coupling from one fluorine to only two of the four apical cyclopropyl protons. When F_a in 58a was irradiated, the doublet signal for the methine cyclopropyl protons collapsed to a broad singlet ($W_{1/2}$ = 3.9 Hz), as expected, and no change was observed in the complex pattern for the apical cyclopropyl protons. However, when F_b was irradiated, the $W_{1/2}$ for the methine cyclopropyl doublet decreased to 2.4 Hz as expected (note that this again indicated small coupling to the bridgehead protons), but of more interest was the change in the spirocyclopropyl proton signals. The upfield

group of three broadened lines, which remained unchanged when either F_a or F_b was irradiated, were assigned to the two protons anti to the gem-difluorocyclopropyl group and situated above the double bond. The downfield group of six broad lines collapsed to three lines when the F_b coupling was removed, and measurement of $J_{F_bH_{syn}}$ placed a value of 4 Hz on this long range $^{19}F - {}^{1}H$ coupling. If 58a were endo (that is, 58), as depicted below, with the observed J_{FH} outlined, the alternate long range coupling



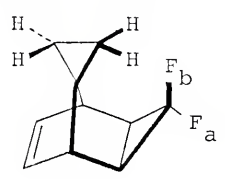
58

"observed" $J_{F_bH_{syn}}$



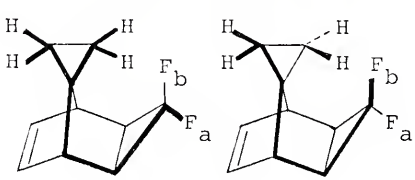
alternate, unobserved J_{FH}

as either $J_{F_bH_{anti}}$ or even $J_{F_aH_{anti, \text{ or } syn}}$, should at least have been observed in the decoupling experiment. Similar analysis for the proposed exo structure 58a, as shown below, reveals that F_b is in much closer proximity to the syn protons, to which it is coupled, than F_a, which is



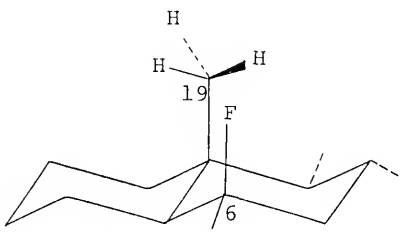
58a

"observed" $J_{F_bH_{syn}}$

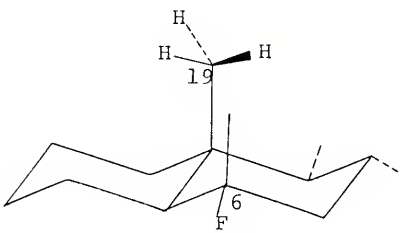


alternate, unobserved J_{FH}

situated away from both the syn and anti spirocyclopropyl protons. All of these observations can be correlated by the application of an empirically derived rule stemming from observations of long range ^{19}F - ^{1}H coupling made by Cross et al.[56,57,58] For example, the observance of five bond coupling in 6-fluorosteroids is dependent on whether the ^{19}F atom is α or β, as shown below. In 59, the $-CH_3$

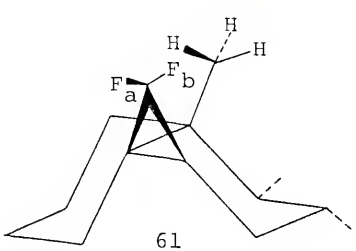


59 (6β-F)

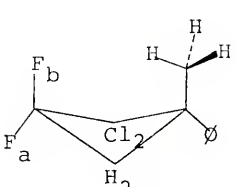


60 (6α-F)

resonance appears as a doublet, whereas in 60, no observable coupling of this type occurs. Also, in the 5β, 6β -difluoro-cyclopropyl steroid 61, the methyl resonance is a doublet, indicating coupling to one, but not both, of the gem-fluorines, which is rather analagous to the situation seen for the exo compound 58a. Finally, in the cyclobutane 62, only F_b is observed to be coupled to the methyl group (which is in accord



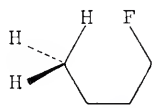
61



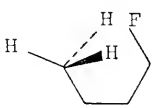
62

with the previous data if the conformation shown above is strongly preferred).

All of the above data were condensed into a rule, useful for predicting long range ^{19}F - ^{1}H coupling, which states that "^{19}F - ^{1}H coupling will be observed only when a vector directed along the C-F bond and originating at the carbon atom can converge upon and intersect a similar vector directed along a C-H bond of the methyl group."[59] In fairness, this rule is not totally applicable to 58a, since the C-F_b vector bisects the angle formed by H_{syn}-C-H_{syn}, and does not directly intersect either C-H vector. However, since this coupling is most likely a through-bond effect, the simple convergence of the C-F_b and C-H_{syn} vectors may make the use of the rule justifiable for 58a. The six bond coupling that we observed in 58a is, in our opinion, the first example of the type of long range J_{FH} designated by Jefford[60] as "intercalated". That is, in the intercalated arrangement the C-F vector bisects the H-C-H angle (as in 58a), whereas in the "opposed" mode, the C-F and C-H vectors intersect. The intercalated and opposed orientations as designated by Jefford[60] for $^{5}J_{FH}$ are shown below.

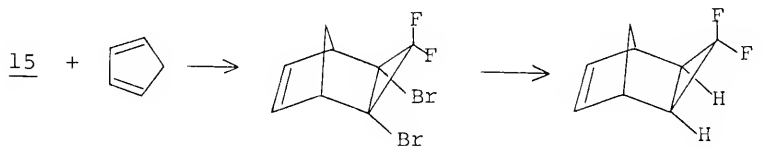


opposed



intercalated

A third indication of exo stereochemistry in 58a comes from comparison of the ^{19}F nmr chemical shifts for 57a and 58a with the reference system obtained from the [4 + 2] cycloaddition of 1,2-dibromo-3,3-difluorocyclopropene (15) with cyclopentadiene, which at room temperature gives only the exo adduct 63, which can be converted to 64 (also exo) by the use of tri-n-butyltin hydride, as shown. (The arguments for exo structures 63

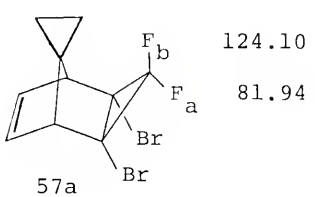


63 64

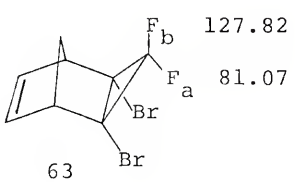
and 64 will be given later and in relation to data from other reactions.) The comparative ^{19}F nmr chemical shift data are shown in Table VIII. What is pertinent is the

Table VIII

Comparison of ^{19}F Nmr Chemical Shift Data

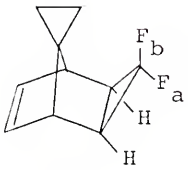


57a 124.10 81.94



63 127.82 81.07

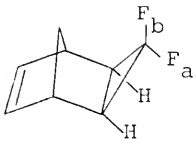
Table VIII - Continued



131.72

100.30

58a



139.32

100.12

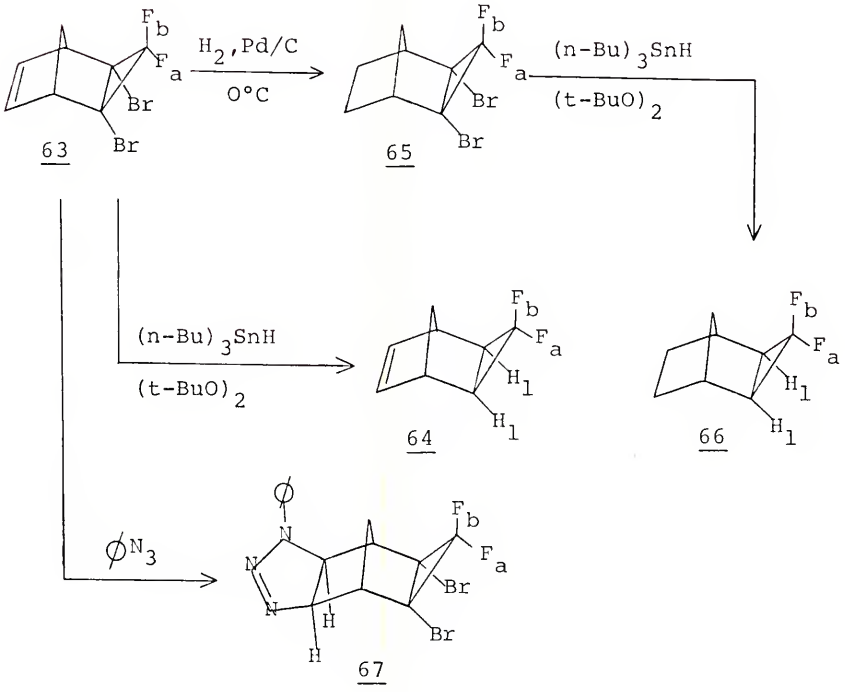
64

similarity in δF_a for 57a and 63, and 58a and 64, which in turn indicates the similarity of the environments for F_a in these compounds. The much larger discrepancies for δF_b in 57a and 63, and 58a and 64 are due to the differences in the bridge substituents in the two systems. In summation, then, 57a and 58a appear to be the most probable structures for the cycloadduct of 15 and 56, and for the product derived from the reduction processes, even though on steric grounds the endo structures (57 and 58), in analogy to the cyclopropene adduct of 56, were thought to be the more likely of the two isomeric possibilities.

As mentioned above, the [4 + 2] cycloadduct 63 of 15 with cyclopentadiene was prepared in CCl_4 at room temperature. At first, the crude reaction mixture was catalytically reduced to 65 to prevent decomposition, but subsequently it was found that 63 could be purified by distillation at reduced pressure and fully characterized. In addition, both 65 and 63 were treated with tri-n-butyltin hydride producing 66 and 64, respectively. Finally, the phenyl azide adduct (67) of 63, was prepared. These transformations are illustrated in Scheme

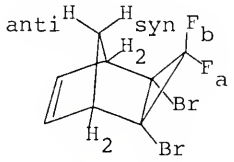
VI. The exo stereochemistry of 63, 64, 65, 66, and 67

Scheme VI



was unambiguously established by an authentic synthesis of 66, to be discussed later. The ^{1}H nmr and ^{19}F nmr spectra of 63 exhibited some unusual features worthy of detailed analysis. As expected, in the ^{19}F nmr spectrum F_a appeared at lowest field as a doublet ($W_{1/2}$ = 3.6 Hz; $J_{F_aF_b}$ = 145.5 Hz), and in accord with earlier observations was assigned the position cis to the methine cyclopropyl bromine atoms. This assignment was confirmed in the usual manner after reduction with tri-n-butyltin hydride. On the other hand, the

F_b resonance, at highest field, was a doublet ($J_{F_aF_b}$) of quartets of doublets. The quartet coupling was 3.2 Hz and the doublet coupling was about 1.2 Hz. Coupling of 3 Hz from F_b to the bridgehead protons (H_2) agrees with our earlier data, and an additional (and coincidental) coupling of 3 Hz from F_b to H_{syn}, as shown below, is also reasonable when the long range coupling discussed earlier is considered and the "C-F vector- C-H vector" rule is recalled. This argument leaves only a 1.2 Hz coupling to



63

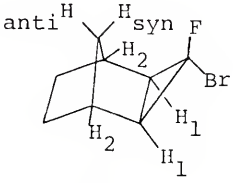
$J_{F_bH_2} \sim J_{F_bH_{syn}} = 3.2$ Hz

$J_{F_bH_{anti}} = 1.2$ Hz

F_b to be accounted for, and the most likely mode of coupling is the five bond coupling $J_{F_bH_{anti}}$, as shown above. Turning to the ^1H nmr spectrum of 63, the assignment of the low field half of the bridge protons' AB system at $\delta 2.02$ to H_{anti} and the high field half at $\delta 1.32$ to H_{syn} is based on the expected shielding of H_{syn} by the cyclopropane ring. The doublet for H_{anti} had a $W_{1/2} = 4$ Hz with $J_{H_{syn}H_{anti}} = 9.6$ Hz. The signal for H_{syn} appeared as a doublet of doublets of triplets. As before, $J_{H_{syn}H_{anti}} = 9.6$ Hz, and $J_{F_bH_{syn}} = 3.2$ Hz, leaving only the triplet coupling to be accounted for by $J_{H_{syn}H_2} = 1.8$ Hz. Also, in a decoupling experiment, when the

H_2 signal was irradiated, the triplet $J_{H_{syn}H_2}$ coupling was removed, leaving a doublet ($J_{H_{syn}H_{anti}}$ = 9.6 Hz) of doublets ($J_{F_bH_{syn}}$ = 3 Hz) for the H_{syn} resonance. The long range ^{19}F - ^{1}H coupling detailed above was also visible throughout the series 63 - 67 whenever the signal for H_{syn} was separated from the rest of the spectrum.

These findings are somewhat in contrast to long range ^{19}F - ^{1}H coupling data reported for the analagous compound 71 by Jefford et al.[60] According to their analysis of the ^{19}F nmr and ^{1}H nmr spectra of 71, the following coupling constants were assigned. No mention was made of any coupling



71

$J_{FH_{syn}}$ = 3.6 Hz
$J_{FH_{anti}}$ = 3.0 Hz
J_{FH_1} = 3.5 Hz

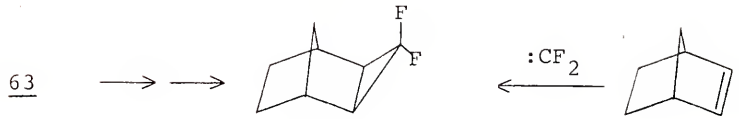
from the fluorine to the bridgehead protons (H_2), which is odd since in our adduct 63, $J_{F_bH_2}$ was found to be 3.2 Hz. Moreoever, the assignment of $J_{FH_{anti}}$ = 3.0 Hz in 71 also disagrees with our assignment in 63 of $J_{F_bH_{anti}}$ = 1.2 Hz. Of course, 63 is an unsaturated system, whereas 71, as a saturated analog, could differ enough in geometry to cause substantial changes in values for long range J_{FH}.

In summarizing the results of the cycloadditions of 1,2-dibromo-3,3-difluorocyclopropene (15) with cyclic 1,3-dienes, it becomes necessary to state explicitly what was

merely implicit in the preceding discussion. That is, in all cases the products that have been characterized represent isolated, purified substances, which of necessity must comprise less than the amount of material which would result from 100% conversion of starting materials. Also, most of the reactions were run under conditions highly conducive (as will be discussed shortly) to endo-exo isomerizations. As a prime example, in the debromination of the 1,3-diphenylisobenzofuran adduct (38a/38), the minor endo component (38) was either isomerized to the exo compound (38a), or the endo debrominated species was not isolated during the workup of the reduction mixture. Therefore, the formation of minor amounts of endo cycloadducts with 15 is not ruled out for any of the cycloadductions and in some cases their actual formation was confirmed (see Chapter II, section III. Isomerization Studies of Selected [4 + 2] Cycloadducts, p 80).

Carbene Additions to the Bicyclo-[2.2.1]-heptyl System

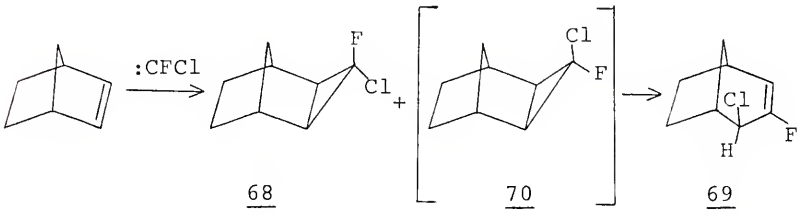
The proof of structure for our Diels-Alder adduct 63, previously alluded to, consisted of conversion of 63 to 66, the saturated, debrominated fluorocarbon. It was noted that this same material, if it were exo, should be accessible by way of addition of difluorocarbene ($:CF_2$) to norbornene. This reaction was carried out using the procedure developed by Seyferth et al.[61] for generating difluorocarbene (which most likely exists as a carbenoid). The material isolated from the difluorocarbene addition to norbornene had an



66

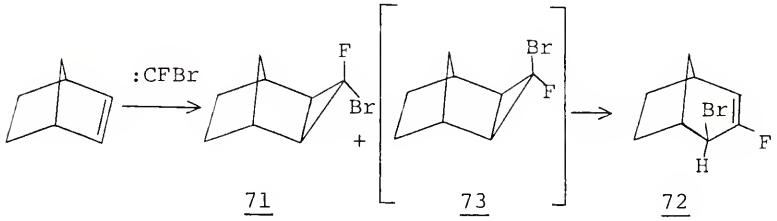
infrared spectrum identical to the infrared spectrum of 66 which was derived from the cycloaddition product of 15 with cyclopentadiene (see Scheme VI).

At this point a brief discussion of carbene additions to the bicyclo[2.2.1]heptyl system is in order. When a carbene adds to norbornene, the sole product is the result of exo addition,[62,63] due presumably to the steric hindrance to the endo pathway by the endo-5,6-hydrogens. There have been reports of halocarbene additions to norbornene, and in those cases where one or both of the halogens were fluorine, the thermally stable products (i.e, non ring-opened) were found to be exclusively exo. For example,[64] fluorochlorocarbene (:CFCl), produced by the base catalyzed decomposition of sym-difluorotetrachloroacetone, gave two products, 68 and 69, with 69 arising from the rearrangement of 70.



68 70 69

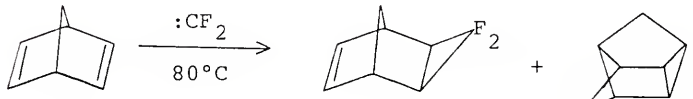
Similarly, bromofluorocarbene (:CFBr) gave the analagous products 71 and 72 (with 72 derived from 73.)[44] With



71 73 72

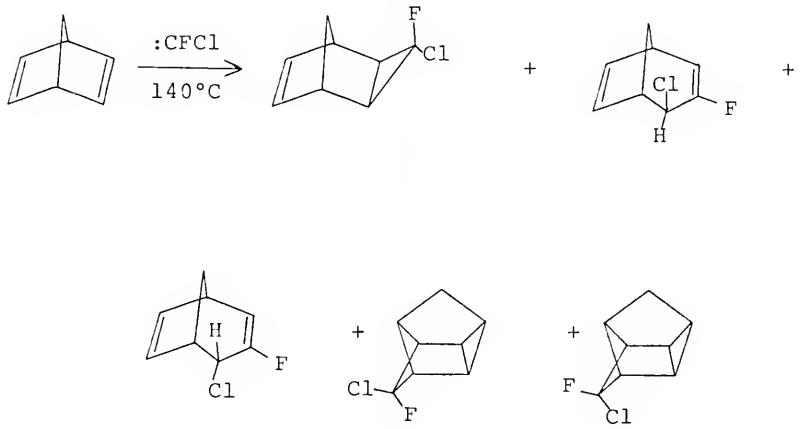
norbornadiene the steric inhibition to endo carbene addition is diminished and endo addition products with methylene have been reported.[65,66,67,68,69] Halocarbene additions to norbornadiene would likewise be expected to give mixtures of exo and endo products. Two recent papers by Jefford and coworkers,[70,71] dealing with the results of fluorocarbene additions to norbornadiene, not only confirmed the possibility of endo addition in this system, but provided ^{1}H nmr data that proved quite useful in making stereochemical assignments in related tricyclic systems.

In the first paper,[70] exposure of norbornadiene to difluorocarbene (generated at 80° C) resulted in isolation of only two products, 74 and 75. Also, when norbornadiene was reacted with chlorofluorocarbene (:CFCl) at 140° C, five



74 75

products were isolated, as shown below. The absence of any endo-tricyclo[3.2.1.$0^{2,4}$]octyl compounds is not surprising

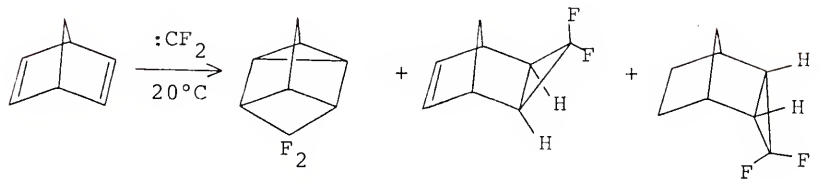


in view of the stringent reaction conditions (140° C, 12 hours), as compared to Jefford's later paper,[71] which recounts the results of the reaction of norbornadiene with difluorocarbene at 20° C.

In a series of experiments performed at 20° C, that is, under conditions non-conducive to isomerization of any of the reaction products, Jefford was able to separate and characterize the difluorocarbene adducts of norbornadiene and to compare them to the analagous adducts of 7-methyl-norbornadiene. ^{1}H and ^{19}F Nmr chemical shifts and ^{1}H - ^{19}F long range coupling data enabled the structures of all products to be assigned with some degree of certainty.

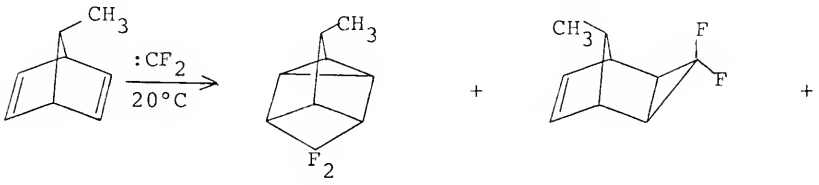
Norbornadiene and difluorocarbene, at 20° C, form three 1:1 adducts; a homo-1,4-adduct (75), plus exo (74)- and endo

(76)-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene.

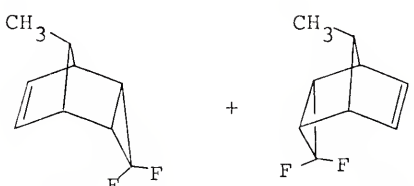


75 74 76

Similarly, 7-methylnorbornadiene forms four adducts with difluorocarbene; a homo-1,4-adduct (77), as well as the exo-anti (78)-, endo-anti (79)-, and endo-syn (80)-3,3-difluoro-8-methyltricyclo[3.2.1.$0^{2,4}$]oct-6-enes, as shown below. Accurate structural assignments in these tricyclic



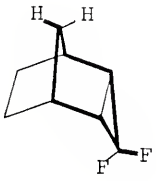
77 78

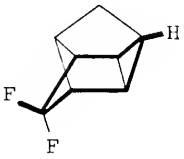


79 80

adducts were expedited by the presence or absence of long range ^{19}F - ^{1}H coupling, labelled $^{5}J_{FH}$ by Jefford, amounting to 8.5 Hz, and present only in those compounds having the

requisite structural features, namely, an endo-gem-difluorocyclopropane ring and a proton on the bridge anti with respect to the cyclopropane ring. Similar long range ^{19}F - ^{1}H coupling (9.8 Hz) was also observed in the tetracyclic products 75 and 77, due to the presence of the same chair cyclohexane 1,4-diequatorial ^{19}F - ^{1}H arrangement, as shown below. Only the endo tricyclic adducts 76 and 80 display long range ^{19}F - ^{1}H coupling of this magnitude.



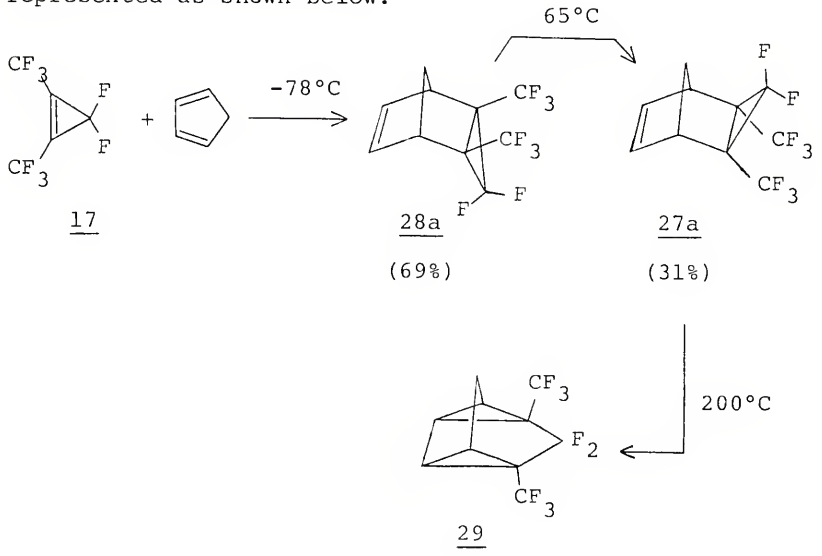


The lack of $^{5}J_{FH}$ in 79 is due, of course, to the presence of the anti methyl group.

If the data presented by Sargeant[31] for the cycloaddition of 1,3-bis(trifluoromethyl)3,3-cyclopropene (17) with cyclopentadiene, which was discussed earlier (see Introduction, section III. Perhalocyclopropenes as Dienophiles, p 12), is now reexamined with regard to long range ^{19}F - ^{1}H coupling, it becomes apparent that the two epimeric cyclopentadiene adducts of 17 should indeed be assigned the structures 27a and 28a, as we had suspected earlier. This reversal of the assignments made by Sargeant is based on the fact that only 28a (endo) exhibits a $J_{F_aH_f}$ of 8.5 Hz, and thus our earlier revision of the exo and endo assignments

was entirely in order.

As a part of this same work,[71] Jefford also studied the thermal behavior of 74 and 76, and found that endo-76 isomerized at 60° - 80° C to exo-74. Therefore, the fact that we isolated only the exo adduct 63 of cyclopentadiene and 15 by distillation is reasonable. Further, as Jefford points out, the facile isomerization of 76 to 74, plus the observation of the 8.5 Hz ^{19}F - ^{1}H coupling in 76 only, leads inevitably to a reassessment of the isomerization work done by Sargeant[31] discussed earlier. Again, as we had suspected, the reassignment of the stereochemistries of Sargeant's Diels-Alder adducts to 27a and 28a now makes their thermal behavior also seem more chemically sound. Thus, the reaction of 17 with cyclopentadiene and the subsequent isomerizations of the products is most correctly represented as shown below.

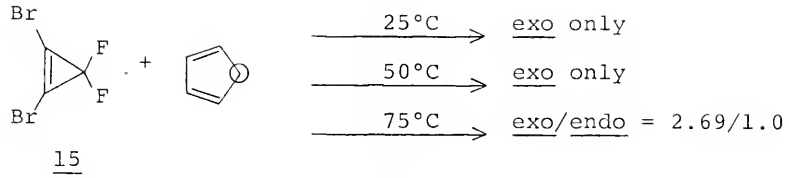


17 28a (69%) 27a (31%) 29

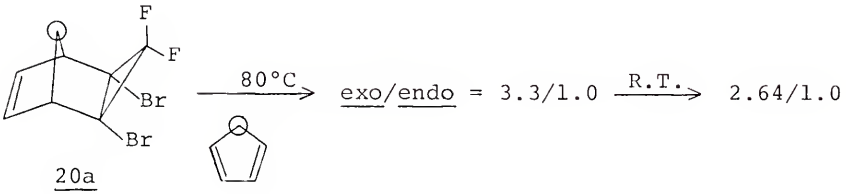
Isomerization Studies of Selected [4 + 2] Cycloadducts

The observation of endo to exo isomerization (76 74) by Jefford[71] under relatively mild conditions (60° - 80° C) prompted us to reinvestigate the behavior of 20a under comparable conditions. Our approach to the problem was twofold; first, the reaction of 1,2-dibromo-3,3-difluorocyclopropene (15) with excess furan was run at 25°, 50°, and 75° C. The crude reaction mixtures were then examined using ^{1}H nmr for completeness and by ^{19}F nmr for the detection of the exo (20a) and endo (20) isomers. The structure for endo 20 was evident from the ^{1}H and ^{19}F nmr data (see Table IX). The ^{1}H nmr spectra for exo 20a and endo 20 appear to be identical, and the ^{19}F data for endo 20 are consistent only with an unrearranged tricyclic structure with $J_{F_aF_b}$ = 143.0 Hz, and $J_{F_bH_2}$ = 2.2 Hz. Second, a sample of 20a, verified by ^{19}F nmr to contain only exo 20a, was heated at 80° C in the presence of excess furan, and the ^{19}F nmr spectrum of the resulting solution was recorded. Also, an nmr sample of the exo isobenzofuran adduct (40) was heated at 80° C for one week and then analyzed by ^{19}F nmr. The results of these experiments are shown in Scheme VII. The failure of the isobenzofuran adduct 40 to isomerize is not too surprising, if the mechanism for exo/endo equilibration consists of a retro-Diels-Alder reaction followed by recombination to give an equilibrium ratio of products. In order for 40 to undergo such a retro-cycloaddition, the

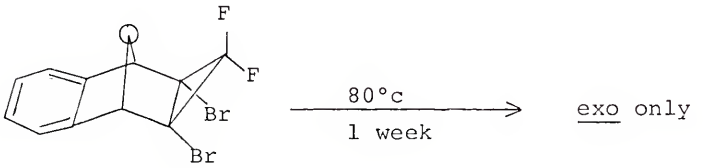
Scheme VII



15



20a



40

aromaticity of the benzo-moiety in 40 would have to be disrupted, so that this pathway would seem to be unlikely to occur with 40.

Second, the likelihood of a retro-Diels-Alder reaction taking place in the 20/20a system is greater than with 40 due to the small gain in aromaticity if furan were formed

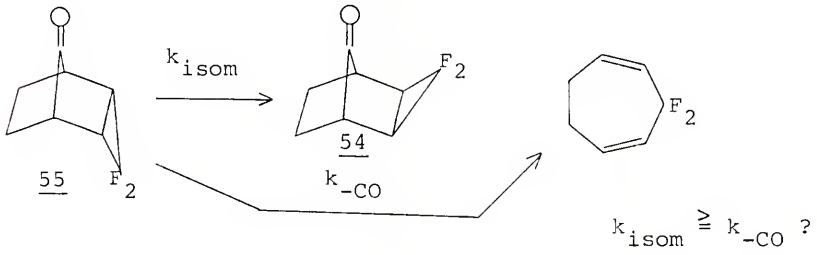
from either stereoisomer by way of the retro-cycloaddition pathway. Thus, a possible mechanistic rationale for the behavior observed for 20a is that this exo isomer, under prolonged heating, isomerizes partially to the endo isomer 20 via retro-cycloaddition to furan and 15 followed by readduction, this process continuing until the 2.7/1.0 exo/endo ratio reflecting the relative thermodynamic stabilities of 20a and 20 is obtained. The kinetic product of this cycloaddition appears to be the exo adduct 20a, since at lower temperatures, 20a was the only product observed in the ^{19}F nmr spectrum.

Since endo-20 is less stable than exo-20a, it is also reasonable to assume that 20 should undergo a retro-Diels-Alder reaction more easily than 20a, which helps to account for the apparent fact that Law and Tobey[35] in their original work did not observe any endo material when they distilled their crude reaction mixture. The exo adduct, being more volatile (and also more stable) was the material that they collected, thus leaving an endo enriched pot mixture, which, of course, could then have isomerized to the equilibrium mixture. The net result of these processes would be a net distillation of only the exo adduct 20a. When we attempted to isolate the endo material by preparative gas chromatography, isomerization on the column (at 100° C) probably occurred, since we were only able to obtain a sample comprised of mostly (~60%) endo material. This sample proved to be stable to further isomerization in the absence of furan and at room

temperature, so that we were able to collect ^{1}H nmr and ^{19}F nmr data for the endo compound 20.

The isomerizations of some of the other adducts of 15 could be studied by similar techniques, were it not for the fact that the dienes, once formed in the retro-cycloaddition, would tend to dimerize rather than re-form Diels-Alder adducts with 15. Also, since the isomerizations of endo adducts to their exo isomers has been shown to occur under mild heating, the isolation and characterization of endo products will be difficult.

Therefore, in our proposed syntheses of the epimeric 3,3-difluorotricyclo[3.2.1.$0^{2,4}$]octan-8-ones, the endo material (55) could well isomerize to the exo isomer (54) before loss of carbon monoxide could occur, as shown below. This possibility would make the study of the decarbonylative



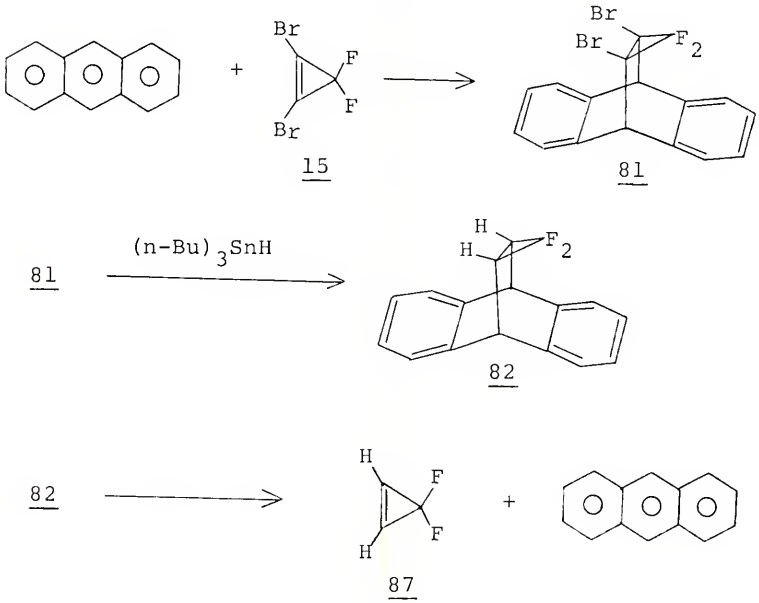
reactivity of 55 and compounds derived from them difficult if the isomerization pathway were dominant.

Synthetic Studies of 3,3-Difluorocyclopropene

One solution to the problem of synthesis of the endo

isomer 55 would be to react 6,6-dimethylfulvene with a gem-difluorocyclopropene having a greater reactivity than 15, so that a lower reaction temperature (more conducive to endo adduct formation) could be used in the initial cycloaddition. The obvious choice for this dienophile is the parent compound, 3,3-difluorocyclopropene (87), which has not yet been reported. We have attempted the synthesis of 87 and one of the more promising synthetic routes we devised is outlined in Scheme VIII. The reaction of 15

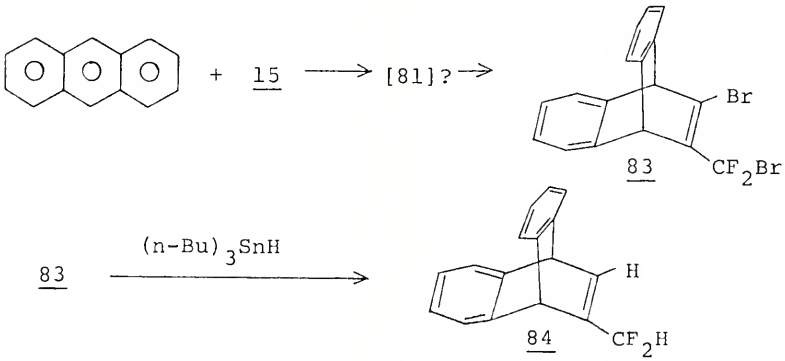
Scheme VIII



with anthracene required prolonged heating at 130° C, increasing the probability of unwanted side reactions. Instead of the desired Diels-Alder adduct 81, we obtained the ring

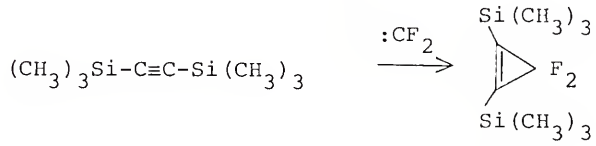
opened isomer 83, which probably arose from the rupture of one of the peripheral cyclopropane bonds after the initial adduction of 15 by anthracene had taken place. The ^{1}H nmr spectrum of 83 consisted of two singlets for the bridgehead protons plus a group of complex aromatic absorptions, while the ^{19}F spectrum consisted of only a singlet at $\delta 47.01$, which is consistent with the ring opened structure but clearly eliminates the original Diels-Alder adduct structure 81. Reduction of the two bromine atoms in 83 could not produce, of course, the desired compound 82, but instead gave the ring opened analog 84. The 100 MHz ^{1}H nmr spectrum of 84 revealed a triplet at 6.1 with $J = 56$ Hz, which is consistent with the presence of a $-CF_2H$ group in the molecule. Also, the remainder of the ^{1}H nmr spectrum, as well as the ^{19}F nmr spectrum supports structure 84. These transformations, that took place instead of the desired reaction sequence above, are shown in Scheme IX. Thus, the ring opening reaction of 81 to give 83 prevented this approach

Scheme IX



from yielding the desired precursor to 3,3-difluorocyclopropene (87).

Another promising approach to 87 required the synthesis of 1,2-bis(trimethylsilyl)-3,3-difluorocyclopropene (86), by the addition of $:CF_2$ to the alkyne 85, as shown below. Hydrolysis of the trimethylsilyl substituents should give

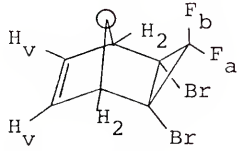
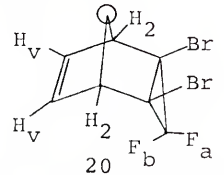
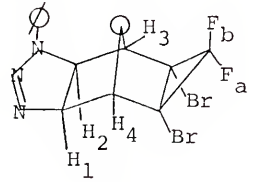


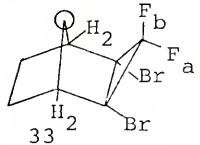
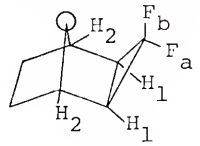
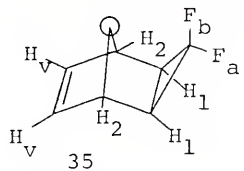
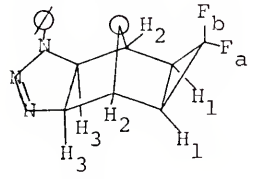
85 86

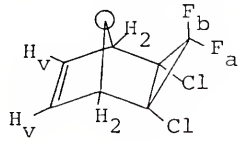
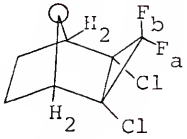
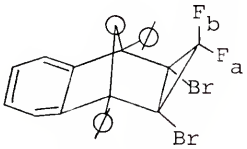
the desired 87. Difluorocarbene addition at 80° C gave an unstable material in low yield that appeared to be 86, but this cyclopropene failed to react with any diene, including isobenzofuran generated *in situ*. Also, an attempted hydrolysis of the trimethylsilyl groups, using a KOH-methanol solution failed to produce 87 or any other volatile products.

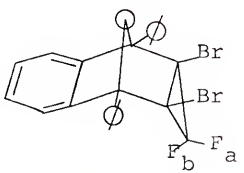
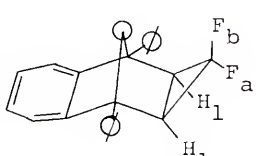
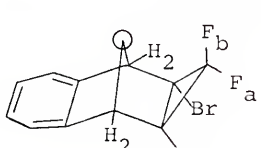
Table IX

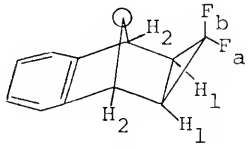
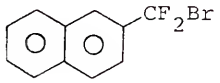
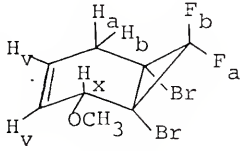
^{1}H nmr and ^{19}F nmr data

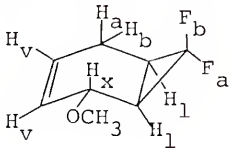
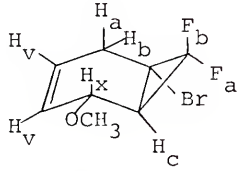
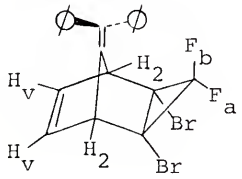
Compound	H(ppm)[a]	mult.[b]	assign.	F(ppm)[c]	mult.	assign.	J(Hz)
 20a	6.78	s	H_v	92.6	d	F_a	$J_{F_aF_b}$=145.5
	5.24	d	H_2	136.2	d of t	F_b	
	[6.81][d]	[s]	[H_v]	[92.0]	[d]	[F_a]	$J_{F_bH_2}$= 2.1
	[5.29]	[d]	[H_2]	[136.5]	[d of t]	[F_b]	
 20	6.78	s	H_v	89.5	d	F_a	$J_{F_aF_b}$=143.0
	5.24	d	H_2	133.9	d of t	F_b	$J_{F_bH_2}$=2.2
 32	7.5-7.0	s(br)+m	ArH	102.8	d of d	F_a	$J_{F_aF_b}$=150.0
	5.60	d	H_1	134.2	d of t	F_b	
	5.17	d	H_4				$J_{F_bH_{3,4}}$=2.1
	4.96	d	H_3				
	4.76	d	H_2				$J_{H_1H_2}$=2.5

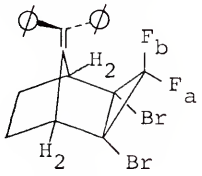
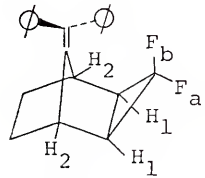
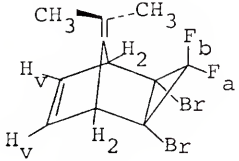
Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 33	4.77	q	H_2	115.9	d of t	F_a	$J_{F_aF_b}$=151.0
	2.35-	q of m	$-CH_2-$	135.5	d of t	F_b	J_{F_aH}=1.7
							$J_{F_bH_2}$=2.2
 34	4.76	q	H_2	127.2	d of t	F_a	$J_{F_aF_b}$=167.0
	1.95	d	H_1(1 of 2)	145.9	d of m	F_b	$J_{F_aH_1}$=13.5
	1.80-	m	$-CH_2-$ +				$J_{F_bH_1}$=1.6
	1.55		H_1(1 of 2)				$J_{F_bH_2}$=2.0
 35	6.58	s	H_v	105.0	d of t	F_a	$J_{F_aF_b}$=156.0
	5.10	q	H_2	143.4	d of p	F_b	$J_{F_aH_1}$=12.0
	1.79	d of d	H_1				$J_{F_bH_1}$=1.5
							$J_{F_bH_2}$=1.5
 36	7.55-	m	ArH(4)	125.0	d of t	F_a	$J_{F_aF_b}$=165.0
	7.30						$J_{F_aH_1}$=13.5
	7.19	sext.	ArH(1)	144.9	d of m	F_b	$J_{F_bH_1}$=1.7
	5.29	AB(q)	H_2				$J_{F_bH_2}$=2.3
	5.14	AB(q)	H_3				
	2.59	d of m	H_1				

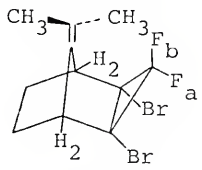
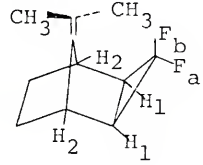
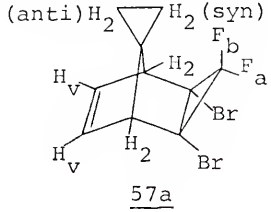
Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 19a	6.84	s	H_v	103.8	d	F_a	$J_{F_aF_b}$=146.0 [147.5]
	5.28	d	H_2	136.7	d of t	F_b	
	[6.87]	[s]	[H_v]	[103.7]	[d]	[F_a]	$J_{F_bH_2}$=2.4 [2.5]
	[5.26]	[d]	[H_2]	[136.7]	[d of t]	[F_b]	
 37	4.78	q	H_2	127.9	d	F_a	$J_{F_aF_b}$=157.0
	2.50-1.65	q of m (AB)	$-CH_2-$	135.4	d of t	F_b	$J_{F_bH_2}$=2.6
 38a	8.00-7.65	m	ArH(4)	93.3	d	F_a	$J_{F_aF_b}$=141.0
	7.65-7.25	m	ArH(10)	129.5	d	F_b	

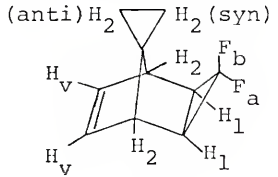
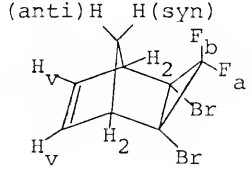
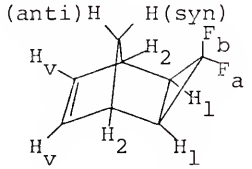
Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 38	——	——	——	99.1 128.1	d d	F_a F_b	$J_{F_aF_b}$=144.0
 39	7.8- 7.3 7.1 2.46	m s d of d	ArH ArH H_1	108.7 142.6	d of t d of t	F_a F_b	$J_{F_aF_b}$=161.0 $J_{F_aH_1}$=12.5 $J_{F_bH_1}$=1.3 $J_{F_bH_2}$=1.5
 40	7.6- 7.0 5.48	m AA'BB' d	ArH H_2	100.9 133.9	d d of t	F_a F_b	$J_{F_aF_b}$=145.0 $J_{F_bH_2}$=2.0

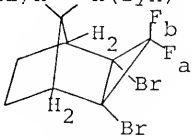
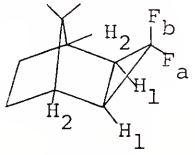
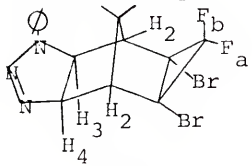
Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 41	7.5-7.07	m AA'BB'	ArH	110.2	d of t	F_a	$J_{F_aF_b}$=165.0
				154.4	d of m	F_b	$J_{F_aH_1}$=12.5
	5.54	d	H_2				$J_{F_bH_1}$=1.4
	1.97	d of d	H_1				$J_{F_bH_2}$=2.0
 44	8.15-7.35	m complex	ArH	43.86	s	$-CF_2-$	———
 46	5.79	q(AB)	H_v	113.9	d of t	F_a	$J_{F_aF_b}$=155.0
	4.34	p	H_x	138.5	d of d	F_b	$J_{F_aH_{a,x}}$=3.2
	3.22	s	$-OCH_3$				$J_{F_bH_2}$=2.4
	3.14	s(br)	$H_{a,b}$				

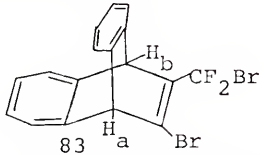
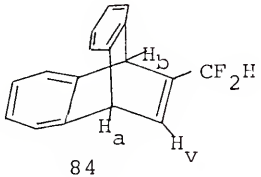
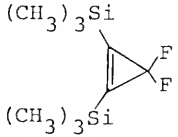
Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 47	5.68	q(AB)	H_v	126.1	d of t	F_a	$J_{F_aF_b}$=163.0
	3.91	m	H_x	151.1	d of m	F_b	$J_{F_aH_1}$=14.0
	3.30	s	$-OCH_3$				
	2.33	q(AB)	$H_{a,b}$				
	1.72	d of q	H_1				
 48	5.72	q(AB)	H_v	97.7	d of d of t	F_a	$J_{F_aF_b}$=161.0 $J_{F_aH_1}$=15.0 $J_{F_aH_{a,x}}$=3.4
	4.16	m	H_x				
	3.34	s	$-OCH_3$	145.5	d of m	F_b	
 51a	7.43-6.88	m	ArH	99.6	d	F_a	$J_{F_aF_b}$=142.5
				130.6	d of t	F_b	$J_{F_bH_2}$=2.5
	6.81	t	H_v				
	3.99	q	H_2				

Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 52a	7.5- 6.9	m	ArH	110.6 136.0	d d of t	F_a F_b	$J_{F_aF_b}$=148.7 $J_{F_bH_2}$=2.8
	3.22	m	H_2				
	2.6- 1.5	m	$-CH_2-$				
 53a	7.18	s(br)	ArH	124.8	d of t	F_a	$J_{F_aF_b}$=161.0
	3.03	m	H_2	142.8	d	F_b	$J_{F_aH_1}$=15.0
	1.9- 1.1	m	$-CH_2-$ $+ H_1$				$J_{F_bH_1}$=2
 51b	6.70	t	H_v	———	———	———	———
	3.93	q	H_2				
	1.53	s	$-CH_3$				

Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 52b	3.13	q	H_2	110.6	d	F_a	$J_{F_aF_b}$=147.0
	2.08	m	$-CH_2-$	136.0	d	F_b	
	1.90	d	+				
	1.8-	s + m	$-CH_3$				
	1.5						
 53b	2.97	m	H_2	124.2	d of t	F_a	$J_{F_aF_b}$=159.0
	2.68	d of d	H_1	146.7	d of m	F_b	$J_{F_aH_1}$=15.0
	1.62	s	$-CH_3$				$J_{F_bH_1}$=2.8
	1.72-	m	$-CH_2-$				
	1.38						
 57a	6.75	t	H_v	81.9	d	F_a	$J_{F_aF_b}$=142.0
	3.10	p	H_2	124.1	d of p	F_b	$J_{F_bH_{syn}}$=4
	1.3-	6 lines	H_{syn}				
	0.8						
	0.6-	3 lines	H_{anti}				
	0.2						

Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 58a	6.72	t	H_v	100.3	d of t	F_a	$J_{F_aF_b}$=157.0
	2.62	m	H_2	131.7	d of m	F_b	$J_{F_aH_1}$=14.0
	1.76	d	H_1				$J_{F_bH_{syn}}$=4
	0.90-0.69	6 lines	H_{syn}				
	0.40-0.20	3 lines	H_{anti}				
 63	6.63	s	H_v	81.1	d	F_a	$J_{F_aF_b}$=145.5
	3.35	sext.	H_2	127.1	d of q	F_b	$J_{F_bH_2}=J_{F_bH_{syn}}$= 3.2
	2.02	d	H_{anti}				
	1.32	d of d of t	H_{syn}				$J_{F_bH_{anti}}$=1.2
							$J_{H_{syn}H_{anti}}$= 9.6
							$J_{H_{syn}H_2}$=1.68
 64	5.45	t	H_v				
	3.20	m	H_2				
	1.73	s(br)	H_1 +	100.1	d of t	F_a	$J_{F_aF_b}$=160.0
	1.50	s(br)	H_{anti}	139.3	d of m	F_b	
	0.98	d of m (1/2 AB)	H_{syn}				$J_{F_aH_1}$=14.0

Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
(anti)H H(syn)  65	2.77	p	H_2	107.0	d of m	F_a	$J_{F_aF_b}$=155.0
	2.2-	complex	$-CH_2-$	121.3	d of m	F_b	
	1.4		$+H_{anti}$				
	1.22	d of m (1/2 AB)	H_{syn}				
(anti)H H(syn)  66	2.59	m	H_2	118.7	d of t	F_a	$J_{F_aF_b}$=163.3
	1.8-	complex	$-CH_2-$		of m		
	1.2		$+H_1$	137.2	d of m	F_b	$J_{F_aH_1}$=15.0
			$+H_{anti}$				
	0.87	d of m (1/2 AB)	H_{syn}				
(anti)H H(syn)  67	7.28	s	ArH	99.8	d	F_a	$J_{F_aF_b}$=154.0
	7.5-6.9	m	ArH	126.2	d of m	F_b	
	5.34	d of s	H_3				$J_{H_3H_4}$=9.5
	4.49	d of d	H_4				
	3.23	d of m	H_2				$J_{H_{syn}H_{anti}}$=
	1.95	d of q	H_{anti}				12.5
	0.95	d of p	H_{syn}				

Compound	H(ppm)	mult.	assign.	F(ppm)	mult.	assign.	J(Hz)
 83	7.5-6.8	complex	ArH	47.01	s	$-CF_2Br$	———
	5.27	s	H_a				
	5.11	s	H_b				
 84	7.44-6.84	m	ArH + H_v	117.1	d of d	$-CF_2H$	$J_{F_2H}=56$ $J_{FH_b}=4$ $J_{H_aH_v}=2$
	6.22	t	$-CF_2H$				
	5.30	d	H_b				
	5.16	d	H_a				
 86	0.25	s	$-CH_3$	102.6	s	F	———

a. all ^1H nmr chemical shifts are reported in ppm downfield from internal TMS. b. abbreviations used; s=singlet, d=doublet, t=triplet, q=quartet, p=pentent, sext=sextet, m=multiplet, br=broad. c. all ^{19}F nmr chemical shifts are reported in ppm upfield from external $CFCl_3$. d. values in [brackets] are from the literature (reference 35).

CHAPTER III

EXPERIMENTAL

General

All melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. All micro analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia.

Infra-red spectra were recorded either on a Beckman IR-10 Spectrophotometer or a Perkin-Elmer 137 Sodium Chloride Spectrophotometer. Solid samples were run as KBr wafers in a Wilkes Mini-Press, and liquid samples were run either between NaCl windows (Neat) or in a Wilkes Mini-Cell with AgCl windows. All ir bands are reported in cm^{-1}, and have been corrected to polystyrene calibration (1601.1 cm^{-1} and 906.5 cm^{-1} reference peaks). Ultra violet spectra were recorded on a Carey-15 UV-Visible Spectrophotometer.

Mass spectra were recorded either on an Hitachi Perkin-Elmer NMR 6E Mass Spectrometer or an Associated Electronics Industries (AEI) Model MS-30 Mass Spectrometer, and were recorded at 70 eV.

Gas chromatography (both analytical and preparative) was performed using a Varian Aerograph 90-P instrument with a thermal conductivity detector.

Proton nmr spectra were recorded on a Varian Associates

Model A-60, 60 MHz nmr spectrometer or a Varian Associates Model XL-100, 100 MHz nmr spectrometer. All ^{19}F nmr spectra were recorded on the XL-100 instrument at 94.1 MHz and all heteronuclear decoupling experiments, as well as Fourier Transform spectra were also done on the XL-100 instrument. All ^{1}H and ^{19}F nmr data, unless quoted in the text of a particular experiment, appear in Table IX.

Preparation of Pentachlorocyclopropane.[26] A five-liter, three-neck round bottom flask was equipped with a mechanical stirrer and a reflux condenser. Trichloroethylene (2.5 l) and 1,2-dimethoxyethane (750 ml) were placed in the flask and brought to reflux. Sodium trichloroacetate (1600 g, 8.63 mol) was added in 200 g portions over a period of about two days. The mixture was stirred and refluxed until CO_2 evolution ceased (usually an additional 24-36 hours). The flask was then cooled and the mixture was filtered to give a blackish-brown solution. After evaporation of excess trichloroethylene and dimethoxyethane, the brown residue was distilled under reduced pressure to give pentachlorocyclopropane (406 g, 22%; bp_{14} 64° - 66° C, lit. bp_7 56° C). Nmr δ3.91 (s, 1H).

Drying the refluxing solution by means of a Dean-Stark tray did not seem to affect the yields. Use of powdered sodium trichloacetate (Eastman, U.S. pellets) increased the reaction rate, but also did not affect the yields.

Preparation of Tetrachlorocyclopropene (11).[27] A one-liter,

three-neck Morton flask was equipped with a paddle blade stirrer, a thermometer, and a reflux condenser. Potassium hydroxide (101.0 g, 1.80 mol) in 120 ml of water was placed in the flask and pentachlorocyclopropane (150.0 g, 0.66 mol) was added. On initiation of vigorous stirring the bright yellow reaction mixture became exothermic. The temperature of the reaction was maintained at 90° - 95° (note 2) by periodic ice-water bath cooling. After about 10 - 15 minutes, the solution abruptly turned yellow-orange, the temperature dropped, and a vapor escaped from the top of the condenser. The stirring and cooling was continued while 150 - 175 ml of water and 75 ml of concentrated hydrochloric acid were added from an addition funnel. Stirring was stopped, and the lower organic phase was drawn off and dried (Na_2SO_4). The aqueous phase was extracted with methylene chloride (3 x 50 ml), and the extracts were dried (Na_2SO_4). The original organic phase and the methylene chloride extracts were combined, the solvent was removed (aspirator) and the residue distilled at atmospheric pressure, under nitrogen, using ice-water cooled receivers and a 6" vigreaux column (microsetup) to give tetrachlorocyclopropene (11) as a clear, colorless, lachrymatory liquid; 50.55 g, 43%; bp 133.0° - 135.5° C, lit. bp 129° - 130° C. The infrared spectrum (Neat, AgCl) showed absorption bands at 1785 (m), 1195 (w), 1150 (s), 1120 (w), 1055 (s), 895 (w), 850 (w), 805 (w), 755 (s), 690 (w) cm^{-1}: lit. 1810 (w), 1300 (w), 1190 (w), 1148 (vs,s), 1100 (w), 1055 (vs,s), 817 (w), 753 (vs,b), 690 (m,s) cm^{-1}.

The best yields were obtained using a Morton flask with a paddle blade stirrer. If the temperature is kept below 90° (85° - 90°) the reaction takes about 15 - 20 minutes, and the yield is lower.

Preparation of 1,2-dichloro-3,3-difluorocyclopropene (14) and 1,2,3-trichloro-3-fluorocyclopropene (13).[28] Tetrachlorocyclopropene (11) (10.3 g, 0.057 mol) and antimony trifluoride (12.6 g, 0.075 mol) were placed in a distillation flask and stirred while gradually heating to a maximum bath temperature of 110° C. Approximately 5 ml of a colorless liquid distilled from 50° - 95° C. Fractionation on a 6" vigreaux column gave 1,2-dichloro-3,3-difluorocyclopropene (14) (2.27 g, 27%, based on tetrachlorocyclopropene (11), bp 54° - 57° C), and a higher boiling fraction (bp 60° - 95°) that by IR analysis contained tetrachlorocyclopropene (11), 1,2-dichloro-3,3-difluorocyclopropene (14) and 1,2,3-trichloro-3-fluorocyclopropene (13) (0.92 g). It was subsequently found that the conversion of tetrachlorocyclopropene (11) to 1,2-dichloro-3,3-difluorocyclopropene (14) could be made more efficient by using the vigreaux column for the original "crude" distillation, and by keeping the bath temperature less than 95° C. In this fashion, 20.6 g tetrachlorocyclopropene (11) gave 6.30 g 1,2-dichloro-3,3-difluorocyclopropene (14) (39%).

Preparation of Tetrabromocyclopropene (12).[28] A three-neck, 250 ml round bottom flask was equipped with a magnetic stirrer,

a 125 ml addition funnel, a reflux condenser, and a nitrogen inlet. Tetrachlorocyclopropene (14) (58.4 g, 0.329 mol) was placed in the flask and boron tribromide (Ventron, 100 g, 0.398 mol) was added with stirring under a nitrogen flow over a 0.5 hour period. The pale yellow solution became warm, and BCl_3 was emitted from the condenser (and was led to the back of the hood). After the addition of boron tribromide was complete, the orange mixture was stirred and swept with nitrogen until the BCl_3 evolution had ceased (ca. 10 - 15 minutes). The volatile components were removed under vacuum (ca. 5 mm Hg) and the residue was distilled giving tetrabromocyclopropene (12) (100.2 g, 87%; bp_{10} 90° - 94° C, lit. $bp_{0.1-0.4m}$ 70° - 95° C). The infrared spectrum (Neat, AgCl) displayed absorption bands at 1760 (m), 1137 - 1120 (d,s), 1077 (m), 1000 (s), 662 (s), 580 (w), 490 (s) cm^{-1}; lit. 1757, 1135 - 1121, 1057, 1002, 664.

Preparation of 1,2-dibromo-3,3-difluorocyclopropene (15).[28] Antimony trifluoride (Fisher, technical grade, 79 g, 0.442 mol) and a stirring bar were placed in a 100 ml round bottom flask. Tetrabromocyclopropene (12) (100.0 g, 0.28 mol) was added and the flask was connected to a distillation apparatus and the mixture was heated to 60° C. In some cases, the initial reaction was quite exothermic, and had to be moderated with an ice-water bath. A white cloudy vapor was given off as heating was continued and the bath temperature was rinsed

until distillation began. After all the distillate (15 - 20 ml) was collected in a round bottom flask cooled by an ice-water bath, it was immediately redistilled under N_2, giving 1,2-dibromo-3,3-difluorocyclopropene (15) (36.6 g, 55.5%; bp 92° - 96° C, lit. bp 105° C). The infrared spectrum (Neat, AgCl) displayed absorption bands at 1727 (w), 1300 (b,s), 1070 (b,s), 823 (m), 717 (w), 549 (w), 512 (w), 479 (w) cm^{-1}; lit. 1724, 1429 (w), 1368 (w), 1304, 1217 (w), 1073, 823, 717 cm^{-1}.

Reaction of 1,2-dibromo-3,3-difluorocyclopropene (15) with Furan-Preparation of 2,4-dibromo-3,3-difluoro-8-oxatricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (20a).[35] Freshly distilled furan (1.5 g, 6.2 mmol) and 10 ml of carbon tetrachloride (Spectrar) were placed in a sealed tube (Fischer-Porter) and heated to 80° for 24 hours. The tube was cooled, opened and the solvent and excess furan were evaporated to yield a dark brown residue which was percolated through a florex column with pentane. Evaporation of the pentane left an orange wax, which on sublimation at reduced pressure (10 - 15 mm Hg, ca. 50° C) gave white needles of 2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (20a) (0.8 g, 43.4%, mp = 61° - 62°, lit. mp = 95°). G.C. examination on a 5', 10% SE - 30 column at 100° showed one peak. The infrared spectrum (KBr) displayed absorption bands at 3015, 1400, 1290, 1235 (w), 1220 (sh), 1190, 1110 (w), 1090 (w), 1020, 1000, 950, 930, 912, 860, 828, 760, 735, 711, 670, 660, 548

cm^{-1}; lit. 3020, 1380, 1295, 1215, 1200, 1020, 1000, 917, 829, 710, 670, 550 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 304 (0.062), 302 (0.115), 300 (0.069), 256 (19.3), 254 (38.6), 252 (20.2), 223 (32.2), 221 (33.4), 155 (98.4), 153 (98.8), 114 (100.0).

Anal. Calcd for $C_7H_4OF_2Br_2$: C, 27.84; H, 1.33; Br, 52.59; F + O, 17.89.

Found: C, 27.84; H, 1.38; Br, 52.39; F + O, 17.39 (diff).

Preparation of Phenyl Azide (31).[72] In a 3-necked, 1 l round bottom flask equipped with an overhead paddle blade stirrer, a thermometer, and a 125 ml dropping funnel were placed 55.5 ml of conc. hydrochloric acid and 300 ml of water. The solution was cooled with an ice-water bath and stirred while phenylhydrazine (33.5 g, 0.31 mol, MCB) was added over 10 minutes, at which time a thick cream colored solid ($ØNHNH_2 \cdot HCl$) precipitated. To this stirred slurry at 0° C was added 100 ml of ether, then $NaNO_2$ (25 g) in 30 ml of water, over a period of 30 minutes with the temperature $\leq 5^{\circ}$ C. The crude mixture was then distilled, and the aqueous azeotrope was collected. When no organic material remained in the pot, the distillation was stopped, and the two phases of the distillate were separated. The aqueous phase was extracted with ether (3 x 50 ml) and the ether extracts were combined with the product. The ethereal solution was dried (Na_2SO_4), the solvent was removed, and the residue upon distillation at reduced pressure gave phenyl azide (31) (23.77 g, 64.4%;

bp_5 49° - 50° C), as a yellow oil which was stored under N_2 at 0° C.

Reaction of 2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (20a) with Phenyl Azide (31).[35] Phenyl azide (31) (0.400 g, 3.20 mmol), 2,4-dibromo-3,3-difluoro-8-oxatricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (20a) (0.955 g, 3.16 mmol) and about 10 ml of CCl_4 (Spectrar) were placed in a sealed tube (Fischer-Porter) and heated to 65° C for four hours. Upon cooling, a brown solid (1.00 g) precipitated, and was filtered. The filtrate was heated at 65° overnight, and a second crop of solid was obtained (0.138 g). The combined solids were recrystallized first from hexane and then from benzene to give the adduct 32 (0.892 g, 67.2%, mp 186° - 187° C). The infrared spectrum (KBr) displayed absorption bands at 1596, 1498, 1476, 1448, 1407, 1390 (sh), 1360, 1310 (w), 1276 (m), 1228 (s), 1180 (sh), 1160 (w), 1120 (br,s), 1103 (sh), 1070 (w), 1040 (w), 1005, 996 (d), 966, 950 (sh), 937 (w), 920 (w), 885 (w), 870 (w), 803, 781, 748, 730, 690 (w), 660 (sh) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 424 (0.50), 422 (1.03), 420 (0.52), 396 (0.12), 394 (0.23), 392 (0.14), 367 (0.6), 365 (1.0), 363 (0.8), 348 (0.3), 346 (0.6), 344 (0.3), 315 (7.6), 313 (7.5), 286 (8.4), 284 (8.6), 265 (6.6), 263 (5.4).

Anal. Calcd for $C_{12}H_9N_3Br_2OF_2$: C, 37.08; H, 2.15; N, 9.98; Br, 37.96; F + O, 12,83.

Found: C, 37.19; H, 2.17; N, 9.97; Br, 38.10; F + O, 12.57 (diff).

Single Crystal X-ray Analysis of Phenyl Azide adduct 32.

The colorless crystals of 32 grown from methylene chloride are monoclinic, space group $P2_1/n$, with a = 6.809(2)Å, b = 13.432(3)Å, c = 15.235(3)Å, and β = 94.010(2)Å. There are four molecules of $C_{13}H_9Br_2N_3OF_2$ per unit cell. Intensity data were measured on a Syntex Pl diffractometer using graphite monchromatized MoK_α radiation and a θ -2θ scan technique. The bromine atoms were located in a Patterson function and the remaining light atoms in a Fourier synthesis. Refinement by full matrix least-squares methods with all atoms anisotropic gave an R of 0.064. The addition of the hydrogen atoms and three additional cycles reduced R to 0.058 for the 1204 reflections with $I \geq 2.0\sigma(I)$ used in the analysis.

The atomic numbering and molecular geometry of 32 are illustrated in Figure I (see p. 37), which clearly establishes exo stereochemistry for both the phenyl azide moiety and the gem difluorocyclopropane ring. The N10-N11 bond length of 1.263(15)Å establishes the position of the double bond. Also, the internal cyclopropane bond (C2-C4) has a length of 1.551(16)Å, longer than either of the peripheral cyclopropane bonds (C2-C3, 1.480(19)Å; C3-C4, 1.487(17)Å.

Preparation of 2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]octane (33). In a 200 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 2,4-dibromo-

3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (20a) (1.51 g, 5.0 mmol), p-toluenesulfonylhydrazine (9.32 g, 50 mmol) diglyme (125 ml), and triethylamine (15 ml). The mixture was stirred and heated (at 80° C) under nitrogen for 8 hours. The mixture was cooled and poured into 200 ml of pentane. A lower dark brown oily layer was drained off and discarded and the pentane solution was washed successively with 5% H_2SO_4, 5% NaOH, and saturated aqueous NaCl solution. The pentane solution was dried (Na_2SO_4, filtered, and the solvent removed. The oily residue was taken up in methylene chloride and washed with water. After drying, the solvent was removed under reduced pressure, giving long white needles (1.35 g, 89% crude). Recrystallization from aqueous ethanol gave white crystals (33) (0.8180 g, 54%). Sublimation gave an analytical sample, mp 56° - 57° C. The infrared spectrum (KBr) displayed absorption bands at 3000, 2963, 1469, 1427 (sh), 1410 (s), 1359 (w), 1313, 1299, 1289 (sh), 1238 (w), 1217 (s), 1189 (s), 1130 (s), 1064, 1029 (sh), 1004, 989, 935, 906 (sh), 901, 834 (s), 829 (sh), 817, 769, 758 (s), 687 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 307 (4.3), 305 (8.9), 303 (4.5), 250 (3.9), 248 (8.6), 246 (4.5), 225 (45.6), 223 (48.3), 198 (47.2), 196 (52.2), 115 (100.0), 96 (49.8).

Anal. Calcd for $C_7H_6Br_2F_2O$: C, 27.66; H, 1.99; Br, 52.58; F + O, 17.76.

Found: C, 27.92; H, 2.01; Br, 52.30; F + O, 17.77 (diff).

Preparation of Tri-n-butyltin Hydride.[73] To a stirred ether (250 ml) slurry of lithium aluminum hydride (6.0 g, 0.15 mol) in a 3-necked round bottom flask equipped with reflux condenser, magnetic stirrer, and a 250 ml dropping funnel, was added under N_2, tri-n-butyltin chloride (38.5 g, 0.118 mol, Aldrich) in 100 ml ether over a period of 20 minutes. The mixture was heated to reflux under N_2 for 2.5 hours, after which the flask was cooled with ice-water, and 0.5 g hydroquinone was added. Then, at 0° C, 12 ml of water was cautiously added, followed by 300 ml of a 20% aqueous solution of potassium sodium tartarate, which resulted in the formation of two phases. The ether phase was separated, the aqueous layer was extracted with ether (2 x 100 ml) and the combined ethereal solution was dried over Na_2SO_4. The solvent was removed under reduced pressure leaving about 50 ml of a colorless solution. Vacuum distillation (caution; the product tends to foam a great deal during distillation) yielded tri-n-butyltin hydride as a slightly cloudy colorless liquid (31.4 g, 72%; $bp_{1.5}$ 90° - 100° C, lit. $bp_{0.7}$ 76° C). The IR spectrum showed a major absorption at 1810 cm^{-1} (Sn-H).

Preparation of 3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]octane (34). 2,4-Dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]-octane (33) (0.395 g, 1.30 mmol), tri-n-butyltin hydride (1.13 g, 3.88 mmol), and a few drops of di-tert-butyl peroxide were placed in a sealed tube (Fischer-Porter) and heated at 90° C for 24 hours. The clear solution was chromatographed on

alumina (MCB 80-200) with pentane. The first twelve fractions (10 ml each) contained alkytin residues. Elution of the product with 1:1 benzene:pentane afforded a yellow oil which on preparative glpc (5', 3% SE-30, T_{col} 95° C, 30 psi) gave a colorless oil (34) (0.122 g, 64%). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3060 (w), 2998, 2960, 2920 (w), 2880, 1676 (w), 1465 (sh), 1442 (s), 1410 (w), 1319 (s), 1298 (w), 1255 (s), 1221, 1208, 1145 (sh), 1130 (s), 1071 (w), 1022 (s), 1012 (sh), 980, 952, 932, 895, 860, 812, 779, 660 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 146 (1.90), 145 (0.58), 128 (1.1), 127 (2.6), 126 (3.2), 125 (4.3), 124 (3.2), 123 (4.3), 97 (54.4), 90 (100.0), 77 (37.2), 39 (27.3).

Anal. Calcd for $C_7H_8F_2O$: C, 57.53; H, 5.52; F + O, 36.95.

Found: C, 57.52; H, 5.61; F + O, 36.87 (diff).

Preparation of 3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (35). In a 10 ml round bottom flask chilled in an ice-water bath were placed 3,3-difluoro-2,4-dibromo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (34) (2.416 g, 16.78 mmol), tri-n-butyltin hydride (5.82 g, 20.0 mmol), and one drop di-tert-butyl peroxide. A magnetic stirring bar was added and the flask was tightly stoppered. The resulting yellow-orange solution was stirred and heated for six hours at 45° C. The volatile product was distilled bulb to bulb, and the

colorless oil purified by preparative glpc (5', 20% SE-30, T_{col} = 110° 20 cc He/min) to yield 0.4378 g of product (35) (38.0%). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3060, 3005, 2985 (sh), 1630 (br,w), 1550 (w), 1415 (s), 1392, 1296, 1250 (s), 1226, 1212, 1130 (s), 1105 (sh), 1080, 1024 (s), 980, 948 (s), 900, 861 (s), 790 (w), 708, 670, 653, 611 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 144 (1.6), 143 (15.2), 115 (74.4), 96 (51.8), 95 (45.0), 75 (40.6), 68 (38.2), 66 (38.0), 55 (48.6), 39 (100.0).

Anal. for $C_7H_6F_2O$: C, 58.33; H, 4.20; F + O, 37.47.

Found: C, 58.45; H, 4.25; F + O, 37.30 (diff).

Preparation of the Phenyl Azide Adduct (36) of 3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (35). In a 10 ml round bottom flask were placed 3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (35) (0.255 g, 1.77 mmol) in 3 ml of carbon tetrachloride. Phenyl azide (31) (0.6 g, 4.0 mmol) in 3 ml of carbon tetrachloride was added and the pale yellow solution was stirred (under nitrogen) magnetically at 50° C. Within 15 minutes, a white precipitate appeared, and after an additional 2 hours, the mixture was cooled and filtered, giving a yellow solid. The product was recrystallized from aqueous ethanol giving 0.0594 g (12.3%) fluffy white needles, mp 204° - 207° (decomposition). Concentration of the filtrate gave an additional 0.210 g for a total yield of 0.269 g (55.6%). The infrared spectrum (KBr) displayed absorption

bands at 3062, 3000, 2919, 1598 (s), 1576 (sh), 1499, 1475, 1440, 1359, 1273, 1260, 1250, 1232, 1217, 1182, 1151, 1137 (sh), 1113 (s,br), 1060, 1009, 981, 968 (sh), 953, 929, 910 (sh), 903 (sh), 882, 839, 800, 748, 712 (w), 698, 685, 660 (sh), 570 (w), 540, 496, 460 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 207 (6.0), 206 (25.0), 186 (22.6), 185 (8.2), 156 (15.0), 143 (9.0), 130 (13.4), 117 (16.6), 115 (6.0), 105 (5.9), 104 (54.1), 103 (6.4), 78 (8.8), 77 (100.0), 51 (31.8), 50 (5.0), 39 (12.0).

Anal. Calcd for $C_{12}HN_3F_2O$: C, 59.31; H, 4.21; N, 15.96, F + O, 20.52.

Found: C, 59.47; H, 4.28; N, 15.91; F + O, 20.34 (diff).

Preparation of 2,4-dichloro-3,3-difluoro-8-oxatricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (19a).[35] In a sealed tube (Fischer-Porter) were placed 1,2-dichloro-3,3-difluorocyclopropene (14) (which had been passed through $NaHCO_3$ with CCl_4, 2.20 g, 15.2 mmol), 5 ml of carbon tetrachloride (Spectrar), and an excess (5 ml) of furan. The tube was sealed and placed in an oil bath at 80° C for 24 hours. At this time, the tube was cooled, opened, the contents concentrated, and then percolated through a florex column with CH_2Cl_2. Evaporation of the solvent left a yellowish oil, which upon distillation at reduced pressure, gave the colorless product 19a as a clear oil that became semisolid at 0° C. The yield was 2.03 g (63%), $bp_{2.75}$ 60° - 61° C. The infrared spectrum (Neat,

NaCl) displayed absorption bands at 3150, 3104, 3022, 1665 (w), 1561 (w), 1436 (s), 1420 (sh), 1400 (s,br), 1350, 1294 (sh), 1255 (sh), 1238 (sh), 1221 (sh), 1205 (s,br), 1114, 1086, 1049 (s), 1030 (s,br), 958, 922 (s), 837 (s), 792 (sh), 782 (s), 741 (s), 726, 678 (s), 665 (sh) cm^{-1}; lit.[35] (CCl_4): 3020 (m), 1430, 1400, 1300, 1215, 1200, 1047, 1030, 920, 834, (780, 740, 722 liquid film), 674, 559 cm^{-1}.

Preparation of 2,4-dichloro-3,3-difluoro-8-oxatricyclo-[3.2.1.$0^{2,4}$]octane (37). In a 50 ml round bottom flask equipped with a magnetic stirrer was placed 2,4-dichloro-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (19a) in 30 ml of absolute ethanol. Palladium-on-charcoal (10%, 0.050 g) was added and the mixture was stirred and cooled to 0^{o} while a dry nitrogen cover was maintained. Then the flask was attached to a hydrogen reservoir, under slight positive pressure. The mixture was stirred under hydrogen for 24 hours at 0^{o} C, at which time an aliquot showed no vinyl ^{1}H resonances in its nmr spectrum. The crude mixture was filtered, and the solvent was removed under reduced pressure to give 0.66 g (77%) of a white, crystalline solid, (37), mp 56^{o} - 57.5^{o} C. The infrared spectrum (KBr) displayed absorption bands at 3030 (sh), 3006, 2999 (sh), 2962, 2920, 2880, 1543 (w), 1468, 1430 (s,br), 1410 (s,br), 1389 (sh), 1357, 1310 (s), 1300 (sh), 1290 (s), 1272, 1222 (s), 1210 (sh), 1196 (s), 1136, 1169 (sh), 1041 (sh), 1021 (s,br), 992 (sh), 936 (s), 892 (s), 830 (s), 812 (s), 771 (s), 679, 623 (s), 540 (s), 450, 351 cm^{-1}. The mass spectrum (70 eV)

showed peaks at m/e (rel. intensity) 216 (0.1), 214 (0.2), 188 (8.5), 186 (14.5), 181 (4.0), 179 (11.4), 167 (38.0), 165 (41.4), 151 (100.0), 131 (45.4), 124 (52.3), 115 (42.8), 93 (43.6), 75 (24.6).

Anal. Calcd for $C_7H_6Cl_2F_2O$: C, 39.10; H, 2.81; Cl, 32.98; F + O, 25.11.

Found: C, 39.13; H, 2.83; Cl, 32.87; F + O, 25.17 (diff).

Dechlorination of 2,4-dichloro-3,3-difluoro-8-oxatricyclo-[3.2.1.$0^{2,4}$]octane (37). In a 3-necked, 50 ml round bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser were placed 2,4-dichloro-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]octane (0.357 g, 1.66 mmol), 10 ml of dry tetrahydrofuran, and 2 ml of tert-butyl alcohol. Sodium metal (0.784 g, 0.034 gat.) was added, the system flushed with nitrogen, and the mixture stirred at 50° C under N_2 for 32 hours. The yellow, cloudy mixture was coarsely filtered using an open Buchner funnel to remove large pieces of Na. A few drops of methanol were added to the solution, followed by pentane (50 ml) and water (100 ml). The mixture was shaken in a separatory funnel to effect layer separation and the aqueous phase was extracted with an additional 50 ml of pentane. The pentane layers were combined, washed with 25 ml of saturated aqueous brine, dried, and the solvent removed under reduced pressure to give a yellow oil. Analysis by ^{1}H nmr showed no starting material, and preparative glpc (5', 3% SE-30, T_{col} 95°, 30 cc He/min) gave a colorless oil, identical by IR spectroscopy to authentic 3,3-difluoro-8-

oxatricyclo[3.2.1.$0^{2,4}$]octane (34).

Preparation of 2,4-dibromo-3,3-difluoro-1,5-diphenyl-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$[oct-6-ene (38a). In a sealed tube (Fischer-Porter) were placed 3,3-difluoro-1,2-dibromocyclopropene (15) (0.500 g, 2.14 mmol), 1,3-diphenylisobenzofuran (0.577 g, 2.14 mmol), and carbon tetrachloride (ca. 10 ml). The tube was flushed with nitrogen, sealed, and placed in an oil bath at 80° C for 12 hours. The resulting pale yellow solution was evaporated to an orange oil, which was percolated through a florex column with methylene chloride. Evaporation of the solvent gave an off white solid, which was recrystallized from hexane, yielding 0.651 g (60.2%) of a white solid, mp 129° - 130° C. The infrared spectrum (KBr) displayed absorption bands at 3060 (vw), 1659 (w), 1595 (w), 1497, 1458, 1446 (m), 1385 (s), 1343 (s), 1318 (w), 1300 (s), 1272 (w), 1200 (s), 1170 (w), 1156 (w), 1100 (sh), 1083 (w), 1028 (w), 1012 (sh), 994, 980 (d,s), 904 (m), 853 (w), 833 (s), 776 (s), 765 (s), 750 (s), 720 (w), 695 (sh), 690 (s), 589 (m), 540 (m) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 505 (1), 504 (1), 503 (2), 502 (1), 489 (1), 487 (2), 485 (1), 426 (13.6), 424 (13.6), 384 (4.2), 382 (8.1), 380 (4.4), 345 (13.0), 287 (19.4), 271 (19.5), 240 (7.7), 239 (9.3), 210 (47.3), 166 (5.8), 153 (8.7), 105 (100.0), 77 (47.3).

Anal. Calcd for $C_{23}H_{14}Br_2F_2O$: C, 54.79; H, 2.80; Br, 31.70; F + O, 10.71.

Found: C, 55.01; H, 2.90; Br, 31.54; F + O, 10.55 (diff).

Preparation of 3,3-difluoro-1,5-diphenyl-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (39). A mixture of 2,4-dibromo-3,3-difluoro-1,5-diphenyl-[6,7]-benzo-8-oxatricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (38a) (2.52 g, 5.00 mmol), tri-n-butyltin hydride (5.82 g, 20.0 mmol), and 3 drops of di-tert-butyl peroxide was placed in a sealed tube (Fischer-Porter) and heated at 100° C for 24 hours. The resulting clear orange oil was chromatographed on alumina (80 - 200 mesh), using hexane to separate the mixture of alkyltin residues and the product. The product fractions were evaporated and recrystallized from hexane to give 0.523 g (30%) of white crystals (39), mp = 115° - 116° C. The infrared spectrum (KBr) displayed absorption bands at 3050 (br), 1595 1595 (w,br), 1490, 1455 (sh), 1443, 1410 (br,s), 1340 (s), 1315 (sh), 1299 (w), 1249 (s), 1227 (m), 1175 (w), 1150, 1127 (s), 1103 (w), 1080, 1050 (sh), 1040, 1020 (w), 990 (br,s), 962 (s), 950, 910 (w), 893 (w), 867 (s), 835, 807, 790 (w), 765 (s), 748 (s), 693 (s), 679 (s), 660 (sh), 650 (m), 560 (m), 523 (m), 480 (w), 410 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 347 (14.1), 346 (51.3), 345 (12.2), 327 (14.6), 326 (7.8), 282 (7.0), 281 (26.9), 280 (6.7), 271 (10.0), 270 (7.6), 249 (19.5), 222 (41.7), 202 (28.4), 192 (19.5), 165 (7.3), 105 (100.0), 77 (29.5).

Anal. Calcd for $C_{23}H_{16}F_2O$: C, 79.75; H, 4.66; F + O, 15.59.

Found: C, 79.61; H, 4.74; F + O, 15.65 (diff).

Preparation of 2,4-dibromo-3,3-difluoro-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (40).[52] 1,4-Bis(2-pyridil)-tetrazine (3.69 g, 14.2 mmol) was dissolved in 50 ml of methylene chloride in a 3-necked round bottom flask (250 ml) equipped with a dropping funnel, condenser, magnetic stirrer and nitrogen inlet. The resulting deep red solution was stirred and chilled to 0° C under nitrogen. 1,2-Dibromo-3,3-difluorocyclopropene (15) (3.32 g, 14.2 mmol) and 1,4-dihydronaphthalene-1,4-endo-oxide (2.05 g, 14.2 mmol) in 50 ml of methylene chloride was added dropwise over a period of an hour. The mixture was stirred for an additional hour, while a small excess of the 1,4-dihydronaphthalene-1,4-endo-oxide was added in methylene chloride to complete decolorization of the solution. The resulting pale yellow solution was evaporated and the resulting yellow solid was chromatographed on alumina (MCB 80-200 mesh) using benzene as elutant. The benzene solution was evaporated and the resulting white solid recrystallized from aqueous ethanol to give 3.62 g (72%) of 40 as a white crystalline solid, mp 108° - 109° C. The infrared spectrum (KBr) displayed absorption bands at 3040, 3000, 1460, 1413 (s), 1392 (s), 1365, 1340, 1276 (w), 1265 (sh), 1220, 1203 (s), 1150, 1087, 1048, 1017, 998 (s), 984 (s), 922 (m), 896 (w), 860 (s), 814 (s), 766 (sh), 750 (s), 696 (m), 654 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 354 (0.2), 352 (0.4), 350 (0.2), 325 (0.4), 323 (0.8), 321 (0.4), 306 (10.2), 304 (22.1), 302 (11.8), 273 (6.8), 271 (7.1), 245 (17.6), 244 (13.8), 243

(17.8), 242 (12.8), 192 (20.0), 164 (100.0), 144 (11.8), 143 (10.5), 82 (14.7), 80 (15.1), 63 (12.8), 56 (16.7), 40 (74.0).

Anal. Calcd for $C_{11}H_6Br_2F_2O$: C, 37.53; H, 1.72; Br, 45.41; F + O, 15.34.

Found: C, 37.47; H, 1.77; Br, 45.33; F + O, 15.43 (diff).

Preparation of 3,3-difluoro-[6,7]-benzo-8-oxatricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (41). A mixture of 2,4-dibromo-3,3-difluoro-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (40) (1.056 g, 3.00 mmol), tri-n-butyltin hydride (3.49 g, 12.0 mmol), and a few drops of di-tert-butyl peroxide were placed in a sealed tube (Fischer-Porter) and heated at 90° C for 24 hours. The resulting mixture was chromatographed on alumina (MCB 80-200). After elution of the alkyltin residues with hexane, the product was eluted with 1:1 benzene:hexane. Evaporation of the solvent and recrystallization of the residue from aqueous ethanol afforded 0.26 g (46%) of 41 as a fluffy white solid, mp = 88.5° - 89.0° C. The infrared spectrum (KBr) displayed absorption bands at 3076, 3036, 1600 (w,br), 1460 (sh), 1421 (s), 1370 (w), 1346 (w), 1289 (m), 1260 (sh), 1251 (s), 1222 (m), 1207, 1189, 1155 (w), 1133 (s), 1119 (m), 1099 (w), 1052 (s), 1015 (w), 996 (s), 990 (sh), 952 (m), 931 (s), 868 (s), 830 (s), 756 (s), 670 (s) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 195 (0.34), 194 (2.4), 193 (2.2), 174 (1.1), 173 (1.2), 147 (15.2), 146 (47.2), 145 (8.2), 115 (52.7), 89 (41.7), 87 (38.3), 73 (100.0), 43 (89.0), 19 (86.3).

Anal. Calcd for $C_{11}H_8F_2O$: C, 68.04; H, 4.15; F + O 27.81.

Found: C, 68.20; H, 4.22; F + O, 27.58 (diff).

Reaction of 3,3-difluoro-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (41) with Triphenylphosphine Dibromide.[55] A 3-necked 50 ml round bottom flask was equipped with a 25 ml addition funnel, a reflux condenser, a magnetic stirrer and a thermometer. The system was flushed with and a cover of nitrogen was maintained throughout the reaction. In the flask were placed triphenylphosphine (0.92 g, 3.5 mmol) and chlorobenzene (5 ml). The resulting solution was stirred and cooled to 0° C. A solution of bromine (0.56 g, 3.5 mmol) in chlorobenzene (5 ml) was placed in the addition funnel and added to the flask at such a rate that the temperature was below 5° C. A yellow precipitate ($\emptyset_3PBr^+Br^-$) quickly formed. At that time, the mixture was heated to a bath temperature of 100° C, and 3,3-difluoro-[6,7]-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (41) (0.500 g, 2.6 mmol) in chlorobenzene was added. The mixture was stirred and heated at 100° C for 5 hours, at which time an nmr spectrum of the crude mixture showed no starting material remained. Chromatographed on silica gel with benzene, evaporation of elutant and recrystallization of the crude residue from aqueous ethanol gave 0.387 g of a brown solid (57.9%) which by nmr was contaminated with triphenylphosphine residues. Additional purification by chromatography on silica gel with hexane gave a white solid, mp 63° - 64°, which was identified as β-

(Fluorodibromomethyl)-Naphthalene (44). The infrared spectrum (KBr) displayed absorption bands at 3040 (w), 1789, 1624 (w), 1599 (w), 1500 (w), 1466 (w), 1384 (w), 1352, 1280 (s), 1265 (sh), 1229, 1190, 1161 (w), 1114 (s), 1050 (s), 1019 (sh), 966 (sh), 950 (s), 914, 891 (s), 860, 792 (s), 767, 746 (w), 610 (w) cm^{-1}. The calculated mass for $[M]^{+}$ is 257.9678 and 255.9712, while accurate mass determination gave 257.9687 and 255.9698, for errors of +3.1 ppm and -1.4 ppm. UV (cyclohexane): λmax (ε); 212 (sh) (1.6×10^4), 228 (3.2×10^4), and 274 (8.2×10^3).

Preparation of 2-methoxy-1,6-dibromo-7,7-difluorobicyclo-[4.1.0]hept-3-ene (46). In a sealed tube (Fischer-Porter) were placed 1,2-dibromo-3,3-difluorocyclopropene (15) (1.99 g, 8.5 mmol, freshly distilled and passed through a $NaHCO_3$ plug in a micropipet), 20 ml of carbon tetrachloride (Spectrar), and 1-methoxy-1,3-butadiene (5.0 g, 59.5 mmol, Aldrich). The tube was sealed and placed in an oil bath at 115° C. The colorless solution gradually darkened, and after fourteen hours, the mixture was black-red. The tube was then cooled, and the contents were rinsed into a round bottom flask with methylene chloride. Evaporation of the solvents left a black oil, which was chromatographed on a basic alumina. The first 100 ml hexane fraction contained no product. Two 250 ml benzene fractions were collected, and evaporated to yield 1.31 g (48.4%) of 46 as a yellow oil. The infrared spectrum (Neat, NaCl) displayed absorption bands at 3042, 2998, 2932, 2905,

2880 (sh), 2825, 1669, 1465 (sh), 1450 (sh), 1442 (s), 1412 (s), 1387, 1340, 1319, 1290, 1209 (s), 1195 (sh), 1155, 1089 (sh), 1047, 990 (sh), 978 (w), 970 (w,sh), 951, 902, 889, 770, 760, 732, 693, 630 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 318 (0.1), 316 (0.2), 314 (0.1), 239 (7.1), 237 (8.7), 207 (25.0), 205 (23.9), 127 (51.3), 81 (100).

Anal. Calcd for $C_8H_8Br_2F_2O$: C, 30.22; H, 2.54; Br, 50.26; F + O, 16.98.

Found: C, 30.42; H, 2.62; Br, 50.11; F + O, 16.85 (diff).

Preparation of 2-methoxy-7,7-difluorobicyclo[4.1.0]hept-3-ene (47). In a 10 ml round bottom flask equipped with a magnetic stirrer were placed, at 0° C, 2-methoxy-1,6-dibromo-7,7-difluorobicyclo[4.1.0]hept-3-ene (46) (1.67 g, 5.25 mmol), tri-n-butyltin hydride (4.58 g, 15.75 mmol), and one drop of di-tert-butyl peroxide. The flask was tightly stoppered, and the mixture was stirred and heated at 50° C for 70 hours. The flask was then cooled to room temperature, opened, and attached to an assembly for bulb to bulb distillation. The reaction mixture was frozen with liquid nitrogen, and the system was evacuated and sealed off. The receiver flask was cooled with a dry-ice/isopropyl alcohol bath. Upon warming to room temperature and gentle heating, a clear, colorless oil distilled. Analysis by ^1H nmr indicated only product and some alkyltin residues (yield of crude material 0.911 g, 0.840 g theoretical yield). An ethereal solution of the

product mixture was separated by preparative glpc (5', 3% SE-30 column, T_{col} = 70° C, T_{inj} = 120° C, 30 cc He/min). The yield of 47 as a clear colorless oil was 0.3558 g (42.4%, low due to partially plugged injection port). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3039, 2982, 2934, 2903, 2822, 2812, 1663, 1469 (s), 1436, 1398, 1347, 1330 (w), 1306 (w), 1284 (s), 1235 (sh), 1211, 1191, 1150 (s), 1127 (w), 1110 (sh), 1088 (s), 1070 (sh), 1023, 970, 930 (sh), 900, 819, 712, 695, 625 (sh), 616 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 160 (6.1), 159 (7.5), 145 (14.4), 132 (28.1), 128 (12.2), 127 (38.2), 110 (20.5), 109 (100.0).

Anal. Calcd for $C_8H_{10}F_2O$: C, 59.99; H, 6.29; F + O, 33.72.

Found: C, 59.90; H, 6.33; F + O, 33.69 (diff).

A trace of a second minor component was also isolated from the gas chromatography and was identified by ^1H and ^{19}F nmr and G.C. - mass spectral analysis to be 47 and 1-bromo-5-methoxy-7,7-difluorobicyclo[4.1.0]hept-3-ene (48) (ca. 1:1). The mass spectrum (70 eV) of the latter showed peaks at m/e (rel. intensity) 159 (18.0), 131 (14.8), 127 (33.0), 109 (10.6), 81 (15.5), 77 (25.0), 63 (100.0).

Preparation of 2,4-dibromo-3,3-difluoro-8-(diphenylmethylene)-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (51a). Diphenylfulvene (4.60 g, 20.0 mmol), 1,2-dibromo-3,3-difluorocyclopropene (15) (5.68 g, 20.0 mmol), and ca. 40 ml of carbon tetrachloride (Spectrar) were placed in a sealed tube (Fischer-Porter) and heated at

120° C for 15 hours. The tube was then cooled, opened, the solvent removed, and the dark residue chromatographed on a Florex column (1" x 10") with pentane. The pentane was evaporated leaving an orange oil, which, when dissolved in a minimum amount of hot hexane, afforded 6.41 g (69%) of (51a) as an off-white solid, mp 153° - 155° C. The infrared spectrum (KBr) displayed absorption bands at 3082 (w), 3050 (w), 3017 (w), 2990 (sh), 1597, 1490, 1442, 1392, 1379 (broad d), 1315, 1295 (broad d,w), 1234 (w), 1220 (sh), 1192 (s), 1155, 1092 (w), 1072, 1012, 974 (s), 829, 780, 770, 748, 721, 711 (sh), 700 (s), 669 (sh), 660, 620, 610 (sh) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 466 (8.3), 464 (15.8), 462 (8.3), 446 (0.12), 444 (0.17), 442 (0.10), 386 (71.9), 385 (18.7), 384 (73.8), 383 (22.5), 366 (5.8), 365 (21.7), 364 (6.8), 363 (22.8), 305 (100), 304 (65.6), 285 (63.5), 284 (72.6), 252 (28.7), 227 (31.2), 207 (26.8), 191 (69.0), 165 (42,4), 126 (39.4), 109 (20.0).

Anal. Calcd for $C_{21}H_{14}Br_2F_2$: C, 54.34; H, 3.04; Br, 34.44; F, 8.19.

Found: C, 54.40; H, 3.12; Br, 34.39; F, 8.09 (diff).

Preparation of 2,4-dibromo-3,3-difluoro-8-(diphenylmethylene)-tricyclo[3.2.1.$0^{2,4}$]octane (52a). In a 300 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 2,4-dibromo-3,3-difluoro-8-(diphenylmethylene)-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (51a) (2.50 g, 5.40 mmol), p-toluenesulfonyl-hydrazine (5.03 g, 27.0 mmol), diglyme (150 ml), and triethylamine (5 ml). The mixture was stirred under

a nitrogen atmosphere and heated at 80° C for 24 hours. The resulting orange solution was poured into an equal volume of pentane. A small oily brown layer settled and was drained off. The pentane solution was washed successively with 5% H_2SO_4, 5% NaOH, and saturated aqueous NaCl. After drying (Na_2SO_4) and removal of solvent in vaccuo, the orange-yellow solid was recrystallized from hexane to yield 1.48 g (58.8%) of 52a as off white crystals, mp 119.5° - 120.5° C. The infrared spectrum (KBr) displayed absorption bands at 3080, 3050, 3020, 2999, 2970, 2943, 2870, 1975 (w), 1803 (w), 1590 (m), 1482, 1437, 1402 (s), 1385 (sh), 1315 (w), 1290 (w), 1258 (m), 1197 (s), 1180 (sh), 1145 (m), 1124 (m), 1105 (m), 1060 (m), 1043 (m), 1022 (m), 986 (m), 959 (s), 820 (m,s), 769 (sharp, m), 739, 711 (m), 692 (s), 651 (w), 620 (w), 600 (w), 580 (w), 522 (m), 460 (w), 448 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 468 (13.8), 466 (28.3), 464 (14.1), 440 (1.6), 438 (2.6), 436 (1.7), 388 (11.6), 387 (38.2), 386 (14.6), 385 (38.5), 307 (54.5), 306 (100.0), 286 (26.2), 278 (20.2), 217 (26.8), 191 (34.5), 143 (21.6), 91 (16.8).

Anal. Calcd for C H Br F : C, 54.10; H, 3.46; Br, 34.29; F, 8.15.

Found: C, 54.15; H, 3.54; Br, 34.10; F, 8.21 (diff).

Preparation of 3,3-difluoro-8-(diphenylmethylene)-tricyclo-[3.2.1.0.^{2,4}]octane (53a). 2,4-Dibromo-3,3-difluoro-8-(diphenylmethylene)-tricyclo[3.2.1.$0^{2,4}$]octane (52a) (0.756 g, 1.63 mmol), tri-n-butyltin hydride (1.43 g, 4.91 mmol),

and 3 drops of di-tert-butyl peroxide were placed in a sealed tube (Fischer-Porter) and heated at 90° C for 24 hours. The resulting clear yellow oil was chromatographed on alumina (MCB 80-200). The first fraction (pentane) contained only alkyl-tin residues (by nmr). The second fraction (benzene) upon evaporation gave a pale yellow oil, which crystallized on standing. Recrystallization from ethanol-water gave 0.116 g (23%) of 53a as a white solid, mp 79.5° - 80.5° C. The infrared spectrum (KBr) displayed absorption bands at 3056, 3000, 2978, 2930, 2915, 2880, 2850, 1592 (m), 1485, 1438 (s), 1410 (sh), 1315 (w), 1297 (m), 1272 (m), 1242 (s), 1180 (w), 1155 (w), 1129 (m), 1109 (s), 1061 (m), 1020 (m), 940, 922 (d), 895 (w), 870 (w), 850 (w), 777 (w,sh), 767 (m), 749 (m), 720 (m), 696 (s), 620 (w), 602 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 310 (2.5), 309 (21.2), 308 (100.0), 290 (3.8), 289 (7.3), 261 (11.3), 260 (20.4), 259 (13.4), 231 (31.6), 180 (26.9), 165 (35.6), 150 (29.0), 91 (17.6), 77 (15.6).

Anal. Calcd for $C_{21}H_{18}F_2$: C, 81.79; H, 5.88; F, 12.32. Found: C, 81.87; H, 5.93; F, 12.20.

Preparation of 2,4-dibromo-3,3-difluoro-8-dimethylmethylene)-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (51b). Dimethylfulvene (3.19 g, 30.0 mmol, Frinton), 1,2-dibromo-3,3-difluorocyclopropene (15) (3.52 g, 15.0 mmol), and 50 ml of carbon tetrachloride were placed in a sealed tube (Fischer-Porter) and heated at 115° C for 12 hours. The resulting dark brown solution was evaporated, and the oily residue was chromatographed on Florex,

and eluted with pentane. Evaporation of the pentane gave (51b) as a yellow iol (3.10 g, 60%). This oil, which was unstable, was immediately reduced.

Preparation of 2,4-dibromo-3,3-difluoro-8-(dimethylmethylene)-tricyclo[3.2.1.$0^{2,4}$]octane (52b). In a 300 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 2,4-dibromo-3,3-difluoro-8-(dimethylmethylene)-hydrazine (25.6 g, 138 mmol), 1,2-dimethoxyethane (200 ml), and triethylamine (25 ml). The mixture was stirred under a nitrogen atmosphere and heated at 80° C for 8 hours. The resulting orange solution was cooled and poured into 300 ml of pentane. A small oily layer settled and was drained off and discarded. The pentane solution was washed successively with 5% H_2SO_4, 5% NaOH, and saturated aqueous brine. After drying (Na_2SO_4) and removal of solvent, the remaining oil was chromatographed on florex using pentane (200 ml) as elutant. Evaporation of solvent and recrystallization from hexane gave 0.793 g (17%) of 52b as white crystals, mp 82° - 85° C. The infrared spectrum (KBr) displayed absorption bands at 2980, 2960, 2920, 2900, 2865, 2840 (sh), 1720 (w), 1465 (sh), 1443, 1413 (s), 1390, 1373, 1295, 1270, 1250 (w), 1200 (s), 1170, 1143 (w), 1115 (w), 1105 (w), 1052, 992, 962 (s), 872 (w), 841 (s), 790 (sh), 742 (s), 702 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 344 (3.1), 342 (6.9),340 (3.5), 317 (3.0), 315 (5.8), 313 (2.9), 296 (3.9), 294 (7.3), 292 (3.9), 282 (0.6), 280 (0.9), 278 (0.5), 263 (22.9), 261 (23.0), 235 (92.9), 233 (100), 218 (18.6), 216 (18.6), 183

(22.8), 167 (18.0), 154 (30.8), 41 (63.2), 39 (31.0), 27 (21.6).

Anal. Calcd for $C_{11}H_{12}Br_2F_2$: C, 38.62; H, 3.54; Br, 46.73; F, 11.11.

Found: C, 38.78; H, 3.67; Br, 46.59; F, 11.06 (diff).

Preparation of 3,3-difluoro-8-(dimethylmethylene)tricyclo-[3.2.1.$0^{2,4}$]octane 53b). 2,4-Dibromo-3,3-difluoro-8-(dimethylmethylene)tricyclo[3.2.1.$0^{2,4}$]octane (52b) (0.342 g, 1.00 mmol), tri-n-butyltin hydride (0.873 g, 3.00 mmol), and a few drips of di-tert-butyl peroxide were placed in a sealed tube (Fischer-Porter) and heated at 90° for 24 hours. The resulting reaction mixture was chromatographed on alumina (MCB 80-200). After elution with 30 ml of pentane, the following five fractions (15 ml) were combined and evaporated. The residue was purified by preparative glpc (5', 3% SE-30, T_{col} = 103° C, 30 psi) to give 0.102 g (56%) of 53b as a white crystalline solid, mp = 58.5° - 59.5° C. The infrared spectrum (KBr) displayed absorption bands at 3047, 2987, 2967, 2946, 2907, 2867, 1439 (s,br), 1363, 1327 (w), 1297, 1278, 1252, 1177 (w), 1142 (sh), 1117 (s,br), 1092 (sh), 1062 (w), 1022, 996, 980 (sh), 926 (br), 876 (sh), 862, 832 (sh), 796 (w), 705, 635 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 184 (0.55), 182 (0.68), 165 (5.2), 150 (24.6), 136 (100), 135 (55.8), 121 (67.5), 110 (26.5), 101 (35.5), 96 (23.5), 75 (14.4), 39 (17.8), 27 (48.8), 26 (40.6).

Anal. Calcd for $C_{11}H_{14}F_2$: C, 71.71; H, 7.66; F, 20.63. Found: C, 71.46; H, 71.74; F, 20.80 (diff).

Preparation of Spiro[4.2]heptadiene (56).[74] In a 1l 3-necked Morton flask equipped with a paddle blade stirrer, a dry ice/isopropyl alcohol condenser, and a 250 ml dropping funnel with a gas inlet tube was condensed 400 ml NH_3, with the aid of a dry ice/isopropyl alcohol bath under the flask. At -70° C, with stirring, Na (11.5 g, 0.500 gat.), in small pieces, was added, resulting in a characteristic deep blue solution. The mixture was stirred at -70° C for 2.75 hours, after which time no Na pieces were seen. Then, still at -70° C, freshly distilled cyclopentadiene (44 g, 0.66 mol) was added dropwise over a period of 35 minutes, after which the blue color slowly faded. When the mixture was pale yellow, ethylene dibromide (94 g, 0.50 mol) was added dropwise at -70° C over 2 hours, resulting in a yellow solution that after stirring at -70° C for 5 hours became green, with the appearance of a yellow precipitate. At this point, most of the NH_3 was allowed to evaporate and ether (250 ml) was added, giving a brown solution. The mixture was filtered and the etheral solution to which 25 ml methanol had been added was carefully washed with water (2 x 200 ml), and dried giving an orange solution. Evaporation of the solvent and distillation gave 35.1 g of a colorless liquid, bp_{100} 56° - 59° C, lit. bp_{100} 57°, which by nmr analysis contained about 23.4 g (50.9%) of spiro 4.2 heptadiene (56) contaminated

with ethylene dibromide. For storage purposes, the distilled material was diluted with carbon tetrachloride (1:1, w:w) and stored at 0° C.

Preparation of 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]-oct-6-ene- 8-spiro -cyclopropane (57a). Spiro 4.2 hepta-1,3-diene (56) (0.736 g, 8.00 mmol) in carbon tetrachloride (2 ml) was added to a carbon tetrachloride (2 ml) solution of 1,2-dibromo-3,3-difluorocyclopropene (15) (0.887 g, 3.79 mmol) containing a trace of $NaHCO_3$. The solution was chilled (0° C) and magnetically stirred during the addition. The 10 ml round bottom flask containing the pale yellow solution was then attached to a reflux condenser with a nitrogen bubbler and the mixture was heated to 50° and stirred. When the ^1H nmr of the reaction mixture showed a constant ratio of product to diene vinyl absorptions (after 4 days), the mixture was cooled and excess diene and solvent were removed at room temperature using a vacuum pump. The resulting light orange oil was chromatographed on a neutral alumina (MCB 80-200) with benzene, then the pale yellow oil was re-chromatographed on silica gel with pentane yielding 0.60 g (49%) of 57a as a colorless oil. The infrared spectrum (Neat, NaCl) displayed absorption bands at 3060, 2980, 2950 (sh), 2910 (w), 2860 (sh), 1649 (m), 1477 (w), 1450 (w), 1430 (w), 1415 (m), 1390 (sh), 1378 (vs), 1309 (s), 1329 (m), 1299 (s), 1289 (sh), 1244 (w), 1208 (sh), 1192 (s), 1185 (s), 1159 (s), 1114 (m), 1090 (sh), 1079 (m), 1052 (w), 1028 (s), 1018 (sh),

1000 (m), 984 (m), 962 (s), 931 (m), 915 (sh), 896 (w), 886 (w), 860 (sh), 856 (m), 809 (w), 790 (m), 764 (s), 738 (s), 719 (m), 686 (w), 660 (m) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 328 (2.0, 326 (4.0), 324 (2.1), 300 (0.47), 298 (0.96), 296 (0.51), 247 (37.1), 245 (38.0), 219 (12.3), 217 (12.2), 166 (100.0), 146 (77.8), 138 (34.5), 91 (32.6), 51 (41.5).

Anal. Calcd for $C_{10}H_8Br_2F_2$: C, 36.84; H, 2.47; Br, 49.03; F, 11.66.

Found: C, 37.02; H, 2.48; Br, 48.89; F, 11.61 (diff).

Preparation of 3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene 8-spiro -cyclopropane (58a). In a 10 ml round bottom flask eqiupped with a magnetic stirrer were placed (with ice bath cooling) 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene- 8-spiro -cyclopropane (57a) (1.78 g, 5.46 mmol), tri-n-butyltin hydride (4.72 g, 16.2 mmol), and one drop of di-tert-butyl peroxide. The flask was tightly stoppered and the mixture was stirred and heated at 60° C for twenty hours. The flask was cooled before opening, and was attached to a short path distillation apparatus. The receiver flask was cooled in a dry ice-isopropyl alcohol bath, and bulb to bulb distillation of the reaction mixture gave 0.447 g of a colorless oil, fairly pure by 'H nmr. Final purification was best effected by preparative glpc (5' x 1/4" 15% PMPE, $T_{col.}$ 100° C, 30 cc He/min), and gave 0.332 g (36%) of 58a. The infrared spectrum (Neat, NaCl) displayed absorption

bands at 3117, 3070, 3060, 3027, 2990, 2979, 2921, 1672 (m), 1551 (w), 1460 (w), 1430 (s), 1412 (s), 1363, 1350 (sh), 1330 (sh), 1310, 1264 (s), 1210 (sh), 1196 (sh), 1189, 1136 (w), 1107 (s), 1086, 1054, 1025, 1000, 980 (w), 961, 942 (s), 912 (w,sh), 907, 867, 834 (w), 813 (w), 792 (w), 781 (w), 769 (w,sh), 740 (w), 712, 659 (s) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 168 (9.5), 167 (10.5), 153 (66.5), 140 (100), 133 (43.1), 91 (89.2), 78 (62.7), 51 (41.5), 39 (57.6).

Anal. Calcd for $C_{10}H_{10}F_2$: C, 71.41; H, 5.99; F, 22.59. Found: C, 71.58; H, 6.03; F, 22.39 (diff).

Preparation of 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]-oct-6-ene (63). In a 25-ml, 3-necked round bottom flask equipped with a nitrogen inlet and a magnetic stirrer was placed 1,2-dibromo-3,3-difluorocyclopropene (15) (2.18 g, 9.32 mmol) in about 5 ml of carbon tetrachloride with a few crystals of $NaHCO_3$. The mixture was stirred under nitrogen at 0° C and an excess (2 ml) of freshly distilled cyclopentadiene was added. The resulting solution was stirred at room temperature and the reaction was followed by gas chromatography (5', 20% SE-30, $T_{col} = 100^{\circ}$). After three days, the reaction mixture was transferred to a one-necked flask which was placed on a rotary evaporator. Removal of excess cyclopentadiene and nmr spectral analysis showed the 1:1 adduct to be present. The crude reaction mixture was percolated through florex (with pentane) and the resulting

solution evaporated to give a colorless oil which yielded two fractions upon vacuum distillation: fraction one (bp_{30-50} 80° - 90°) cyclopentadiene dimer; fraction two ($bp_{2.75}$ 88° - 90°) pure product 63. The infrared spectrum (Neat, NaCl) displayed absorption bands at 3025, 2980, 2918, 1650 (w), 1620 (sh), 1555 (w), 1467, 1435 (sh), 1370 (s), 1340 (sh), 1307, 1255 (sh), 1239, 1212, 1172 (s), 1130 (sh), 1094 (w), 1049 (s), 1010, 989, 948 (s), 825 (sh), 910 (sh), 900 (sh), 879 (w), 932 (w), 809 (s), 802 (sh), 730 (s), 715 (sh), 664 (s), 610 (sh) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 302 (1.5), 300 (3.2), 298 (1.6), 114 (19.8), 75 (6.0), 63 (12.6).

Anal. Calcd for $C_8H_6Br_2F_2$: C, 32.03; H, 2.02; Br, 53.28; F, 12.67.

Found: C, 32.08; H, 2.03; Br, 53.16; F, 12.72 (diff).

Preparation of 3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (64). In a 10 ml round bottom flask equipped with a magnetic stirrer were placed 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (63) (3.6 g, 12.0 mmol), tri-n-butyltin hydride (with ice bath cooling, 7.0 g, 24.0 mmol), and di-tert-butyl peroxide (one drop). The flask was stoppered and the mixture was stirred and heated at 50° for 24 hours. Bulb to bulb distillation of the volatiles gave 0.709 g (41%) of crude product 64, which was purified by preparative glpc (5', 5% SE-30, T_{col} 87° C, 20 cc He/min). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3109, 3063, 3030, 2982, 2919,

1625 (w), 1569 (w), 1556 (m), 1474, 1421 (s), 1409 (s), 1392, 1314, 1270 (sh), 1258 (s), 1220 (w), 1182 (w), 1120 (s), 1056, 1029, 979, 950, 921, 882 (w), 861, 805 (m), 738 (sh), 713, 662 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 142 (59.7), 141 (31.0), 127 (53.9), 122 (12.0), 121 (14.5), 91 (90.0), 78 (73.4), 77 (100.0), 65 (23.4), 51 (33.5), 40 (62.6).

Anal. Calcd for $C_8H_8F_2$: C, 67.59; H, 5.67; F, 26.73. Found: C, 67.69; H, 5.69; F, 26.72 (diff).

Preparation of 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]-octane (65). The crude reaction mixture from a preparation of 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (63) was dissolved in a minimal amount of benzene and 5 ml absolute ethanol, and 50 mg 10% Pd-on-carbon was added. The dark brown mixture was stirred vigorously (magnetic stirring) under an atmosphere of H_2 (excess) overnight at room temperature. Nmr spectral analysis showed no vinyl protons, so the reaction mixture was filtered and percolated through a column of florex with pentane as solvent. The pentane was evaporated, and the residue was analyzed by gas chromatography (5', 3% SE-30, T_{col} 102° C). The third component was isolated on preparative scale affording 65 as a colorless oil (1.0292 g, 36.6% based on starting cyclopropene). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3030 (w), 2970 (s), 2940 (sh), 2910 (sh), 2875, 1665 (impurity), 1485 (w), 1460 (w), 1445 (w), 1402 (s), 1334 (m), 1309 (w), 1294, 1279, 1255 (w), 1244 (w), 1200 (s), 1170 (s), 1132 (w), 1098 (w), 1080 (w), 1062

(s), 1053 (sh), 1038 (w), 1021, 995 (w), 982 (sh), 964 (s), 939 (s), 920 (sh), 890 (w), 871 (w), 805 (w), 705 (w), 751 (w), 739 (s), 712 (w,sh), 702 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 304 (0.3), 302 (0.9), 300 (0.8), 298 (0.3), 276 (0.4), 274 (0.7), 272 (0.4), 223 (51.8), 221 (60.4), 195 (50.6), 193 (52.8), 115 (100), 63 (17.2), 44 (28.3), 39 (52.0), 32 (50.9).

Anal. Calcd for $C_8H_8Br_2F_2$: C, 31.82; H, 2.67; Br, 52.93; F, 12.58.

Found: C, 31.84; H, 2.65; Br, 52.75; F, 12.66 (diff).

Preparation of 3,3-difluorotricyclo[3.2.1.$0^{2,4}$]octane (66). 2,4-Dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]octane (65) (0.72 g, 2.4 mmol), tri-n-butyltin hydride (excess, about 2 g), and a few drops of di-tert-butyl peroxide were placed in a 25 ml round bottom flask and heated at 70° C overnight under nitrogen. The flask was then attached to a short path distillation apparatus. A bulb to bulb distillation under vacuum gave a colorless fraction. Preparative glpc gave 0.0969 g (28%) of 66 as a colorless oil (5', 3% SE-30, T_{col} = 110° C). The infrared spectrum (Neat, NaCl) displayed absorption bands at 3023 (w), 2965, 2880, 1440, 1420, 1302, 1292, 1253, 1190, 1145, 1125, 1070, 1030, 1022 (sh), 1000, 965, 922, 906, 872, 840 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 144 (11.1), 129 (9.2), 116 (15.7), 102 (24.8), 97 (35.7), 90 (100.0), 79 (23.4),

54 (55.3), 39 (31.0), 19 (88.1).

Anal. Calcd for $C_8H_{10}F_2$: C, 66.65; H, 6.99; F, 26.36. Found: C, 66.66; H, 6.91; F, 26.43 (diff).

Reaction of 2,4-dibromo-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (63) with Phenyl Azide (31). In a 25 ml, 3-necked round bottom flask equipped with a nitrogen inlet and a magnetic stirrer were placed 1,2-dibromo-3,3-difluorocyclopropene (15) (1.05 g, 4.48 mmol), carbon tetrachloride (about 5 ml), and a few crystals of $NaHCO_3$. The mixture was stirred, cooled to 0° under nitrogen, and freshly distilled cyclopentadiene (about 2 ml, excess) was added. The resulting solution was stirred at room temperature for two days, after which no cyclopropene remained by gas chromatography (5', 20% SE-30, T_{col} 100° C). The mixture was transferred to a 25 ml round bottom flask and the remaining cyclopentadiene was removed by aspirator vacuum. Then phenyl azide (1.5 g, excess) was added, and the resulting pale yellow solution was stirred at room temperature under nitrogen for three days, after which an nmr spectrum of the resulting brown-red slurry showed no vinyl proton resonances. The solution was filtered giving an off white solid, which when recrystallized from benzene gave white crystals of the adduct 67 (0.3093 g, 16.5%, mp 166° - 167° C with decomposition). The infrared spectrum (KBr) displayed absorption bands at 3059 (w), 2994 (w), 1596 (s), 1580 (sh), 1575 (sh), 1555 (sh), 1497, 1480, 1450, 1399, 1362, 1321 (w), 1300 (sh), 1294 (w), 1275, 1250

(w), 1230 (w), 1209, 1173, 1119, 1103 (sh), 1081, 1068, 1033, 1010 (w), 981, 959, 946, 924 (sh), 909 (sh), 886 (w), 850 (w), 795 (sh), 783 (w), 849 (s), 690, 668 (sh), 645 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 393 (0.2), 392 (0.1), 391 (0.3), 390 (0.1), 389 (0.2), 313 (0.8), 312 (4.7), 311 (1.2), 310 (4.8), 256 (2.4), 254 (5.4), 252 (2.6), 231 (13.6), 230 (10.6), 211 (18.0), 194 (12.7), 192 (12.9), 117 (28.4), 105 (48.2), 77 (100.0), 51 (37.4).

Anal. Calcd for $C_{14}H_{11}N_3Br_2F_2$: C, 40.12; H, 2.65; N, 10.03; Br, 38.14; F, 9.07.

Found: C, 40.09; H, 2.66; N, 10.10; Br, 38.00; F, 915 (diff).

Reaction of Norbornene with Phenyltrifluoromethylmercury and Potassium Iodide.[61] In a 25 ml, 3-necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed norbornene (1.41 g, 15.0 mmol), benzene (approx. 10 ml), phenyltrifluoromethylmercury (1.03 g, 3.01 mmol, Ventron), and dry sodium iodide (2.25 g, 15.0 mmol). The mixture was stirred and refluxed for 15 hours, at which time thin-layer chromatography (Eastman SiO_2/benzene or hexane) indicated no unconsumed phenyltrifluoromethylmercury. The pale yellow mixture was filtered, the filtrate was evaporated to volume of ca. 3 ml, and the residue was separated by preparative glpc (5', 3% SE-30, T_{col} 85°, 20 cc He/min), yielding 66 as a colorless oil (0.119 g, 27.5%). The infrared spectrum

(Neat, NaCl) displayed absorption bands at 3019, 2955, 3895 (sh), 2864, 1480 (w), 1455 (sh), 1444 (sh), 1436 (s), 1414 (sh), 1307 (sh), 1289, 1248 (s), 1185 (w), 1140 (sh), 1120 (s), 1064, 1024, 998, 960, 921, 901 (s), 870, 846, 839 (d) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 144 (13.3), 130 (11.4), 116 (42.4), 104 (25.6), 98 (38.5), 91 (100.0), 79 (69.4), 68 (21.9), 55 (53.7), 40 (39.5), 19 (73.0).

Anal. Calcd for $C_8H_{10}F_2$: C, 66.65; H, 6.99; F, 26.36. Found: C, 66.84; H, 6.91; F, 26.25 (diff).

Thermal Behavior of exo-2,4-dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (20a). Three separate samples of 1,2-dibromo-3,3-difluorocyclopropene (15) were dissolved in carbon tetrachloride (Spectrar), and an excess of furan was added. Sample A was kept at room temperature, sample B was heated at 50° C, and sample C was heated at 75° C. After 5 days, the nmr spectra of the samples at room temperature and at 50° C showed no further change. However, the ^{19}F nmr spectrum of the sample heated at 75° C showed signals for exo 20a as well as for endo (20) (see Table I). The exo/endo ratio was determined to be 2.69/1.00, based on ^{19}F nmr integration. In a separate experiment, a 2:1 mixture of 20a: furan when heated at 80° overnight gave an exo/endo ratio of 3.3/1.0. This nmr sample after sitting at room temperature showed an exo/endo ratio of 2.64/1.0. Isolation of the endo isomer 20 proved to be impractical using column or thin layer

chromatography. However, using gas chromatography (2.5', 3% SE-30, T_{col} 90°, 30 cc He/min), it was possible to isolate a fraction containing exo (20) and endo (20a) in a ratio of 0.74/1.00. Significantly, this ratio remained approximately unchanged (0.68/1.00) when the nmr solution was allowed to stand at room temperature for one week. The 60 MHz ^1H nmr spectrum of this mixture showed no peaks other than the singlet at δ6.8 (H_{vinyl}) and the doublet at δ5.2 ($H_{bridgehead}$), indicating the close resemblance of the ^1H nmr spectra of the two isomers. Also, since the $CDCl_3$ solution was rather dilute, the ^{19}F nmr spectra were run using F.T. to enhance resolution. The resulting values for chemical shifts and coupling constants are given in Table I for 20 and 20a.

Thermal Behavior of exo-2,4-dibromo-3,3-difluoro-8-oxa-[6,7]-benzotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (40). An nmr sample of 40 was heated at 80° for eleven days, after which time the ^{19}F nmr spectrum remained unchanged when compared to the spectrum recorded before heating (see Table I).

^1H nmr $Eu(FOD)_3$ Shift Experiments of 34 and 41. In an nmr tube was placed 3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]-octane (34) (0.019 g, 0.13 mmol) in 500 µl of $CDCl_3$. Solutions of $Eu(FOD)_3$ (200 mg, $Eu(FOD)_3$ in 300 µl $CDCl_3$) was added in 40 µl aliquots, and the ^1H nmr spectrum was recorded after each addition. For each proton signal (H_1, H_2, H_3, and H_4) the change in chemical shifts (Δδ) was measured, and Δδ in Hz was plotted vs. Δvolume of $Eu(FOD)_3$ solution in µl. The

average slope over the linear portion of the graph was calculated for each type of proton (H_1, H_2, H_3, and H_4). A similar experiment using 3,3-difluoro-8-oxa-[6,7]-benzotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (41) was carried out (0.025 g, 0.13 mmol) in 500 µl of $CDCl_3$. The comparative results for 34 and 41 are given in Table VI (p 49).

Attempted Preparation of 2,4-dibromo-3,3-difluoro-[6,7]-[8,9]-dibenzotricyclo[3.2.1.$0^{2,4}$]nona-6,8-diene (81). In a sealed tube (Fischer-Porter) were placed anthracene (0.890 g, 5.00 mmol), 1,2-dibromo-3,3-difluorocyclopropene (15) (1.75 g, 7.47 mmol), and approximately 25 ml of carbon tetrachloride (Spectrar). The tube was capped and heated at 120° C for 4 days, after which nmr analysis of the crude reaction mixture showed approximately 50% of the anthracene remained. Another 1.0 g of cyclopropene was added, the tube was recapped, and the heating was resumed, this time at 130° C. After 3 more days, the nmr of the crude mixture showed no anthracene signals. The dark brown solution was concentrated and eluted through a silica gel column with benzene. Concentration of the first benzene fraction gave 1.94 g (94.2%) of a brown oily solid, which upon recrystallization from hexane gave 0.823 g of hard brown crystals (39.9%) which were 95% pure by nmr. A second recrystallization from hexane gave 0.314 g of analytically pure brown crystals, mp = 94° - 97° C, which proved to be 2-(bromodifluoromethyl)-3-bromo-[5,6]-[7,8]-dibenzotricyclo[2.2.2]octa-2,5,7-triene (83). The infrared spectrum (KBr) displayed absorption bands at 3030, 3026, 3008,

2889 (w), 1616 (s), 1480 (w), 1456 (s), 1321 (w), 1308 (s), 1276 (s), 1214, 1205, 1194, 1182, 1152, 1120 (s), 1099, 1068, 1017 (w), 990 (s), 959 (s), 936 (w), 885 (w), 864 (s), 855 (sh), 820 (s), 782, 758 (sh), 742 (s), 725 (sh), 685, 660, 622 (s), 595, 555, 531, 482 (w), 465 (w), 449 (sh) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 414 (3.1), 412 (6.7), 410 (3.5), 334 (49.5), 332 (50.5), 252 (82.6), 202 (100.0), 200 (74.5), 179 (65.5), 150 (78.9), 127 (30.3), 111 (44.8), 44 (23.4).

Anal. Calcd for $C_{17}H_{10}Br_2F_2$: C, 49.55; H, 2.45; Br, 38.79; F, 9.22.

Found: C, 49.65; H, 2.51; Br, 38.96; F, 8.88 (diff).

Reduction of 2-(bromodifluoromethyl)-3-bromo-[5,6]-[7,8]-dibenzotricyclo[2.2.2]octa-2,5,7-triene (83). In a 10 ml round bottom flask equipped with a magnetic stirrer were placed 2-(bromodifluoromethyl)-3-bromo-[5,6]-[7,8]-dibenzotricyclo-[2.2.2]octa-2,5,7-triene (82) (1.06 g, 2.56 mmol), tri-n-butyltin hydride (2.24 g, 7.68 mmol), and a drop of di-tert-butyl peroxide. The flask was tightly stoppered, and the mixture was stirred and heated at 90° C for 15 hours. The resulting yellow solution was cooled, and careful chromatography on a neutral alumina column with hexane/benzene (1:1 v/v) gave a yellow solid. Recrystallization from hexane gave 0.245 g (37.3%) of crude product which when recrystallized from hexane/methanol gave 0.137 g white flakes, which was homogeneous to thin layer chromatography (silica gel/chloroform; alumina/chloroform; alumina/benzene), mp 137.5° -

138.0° C. This product proved to be 2-(difluoromethyl)-[5,6]-[7.8]-dibenzotricyclo[2.2.2]octa-2,5,7-triene (84). The infrared spectrum (KBr) displayed absorption bands at 3064, 3019, 2964, 1640, 1452 (s), 1368 (s), 1320, 1288, 1244 (w), 1198 (w), 1190 (w), 1164 (sh), 1149 (w), 1107 (w), 1059 (s), 1018 (sh), 994 (s), 970 (sh), 930 (sh), 899 (w), 890 (w), 842, 782, 750 (sh), 738 (s), 655, 620 (w), 590 (w), 537 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 254 (54.6), 233 (6.6), 203 (100.0), 202 (63.5), 178 (12.7), 152 (3.2), 151 (3.3), 102 (5.0), 101 (8.5), 87 (3.2), 76 (3.2).

Anal. Calcd for $C_{17}H_{12}F_2$: C, 80.30; H, 4.76; Br, 0.00; F, 14.94.

Found: C, 80.40; H, 4.75; Br, 0.00; F, 14.85 (diff).

Preparation of Bis-(trimethylsilyl)-acetylene (85).[75] In a 3-necked 1l Morton flask immersed in a dry ice/isopropyl alcohol bath, equipped with a high speed stirrer (Lab Line) and a 250 ml dropping funnel was placed Li (4.86 g, 0.17 gat) from freshly cut Li wire. The system was swept with nitrogen, then at -70° C, with stirring, was added trimethylsilyl chloride (32.6 g, 0.30 mol) in 200 ml dry tetrahydrofuran over a half hour. Then tetrachloroethylene (16.58 g, 0.10 mol) in 20 ml of tetrahydrofuran was added at -70° C over a half hour. The mixture was stirred rapidly (ca. 40% of stirrer capcaity) at -70° for 48 hours. The crude mixture was then allowed to warm to room temperature, and the contents of the flask were filtered. The resulting colorless, cloudy

solution which, when distilled at atmospheric pressure under nitrogen, gave bis-(trimethylsilyl)-acetylene (85) (12.00 g, 70.1%; bp 120° - 137° C, lit. bp 134° - 136° C. The nmr spectrum showed a sharp singlet at δ0.16 ppm.

Preparation of 1,2-bis-(trimethylsilyl)-3,3-difluorocyclopropene (86). In a 50 ml round bottom flask were placed bis-(trimethylsilyl)-acetylene (1.53 g, 9.00 mmol), benzene (15 ml), phenyltrifluoromethylmecury (1.03 g, 3.01 mmol), and NaI (1.35 g, 9.01 mmol). The mixture was stirred under nitrogen and heated to reflux for 7 days. The resulting dark mixture was cooled and filtered, and the solvent was removed under reduced pressure, giving a brown residue which by nmr analysis contained some product. The 1,2-bis-(trimethylsilyl)3,3-difluorocyclopropene (86) was purified by preparative gas chromatography (5', 3% SE-30, T_{col} 75° C, 40 cc He/min, T_{inj} 100° C) as a colorless oil (0.1209 g, 18.3%), which polymerized at room temperature. The infrared spectrum (Neat, NaCl) displayed absorption bands at 2961, 2900, 1775 (w), 1710 (w,br), 1662 (sh), 1650 (sh), 1649 (sh), 1410 (w), 1252 (s), 1182, 1019 (s), 872 (sh), 845 (s), 802 (w), 755, 700 (w), 680 (w) cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (rel. intensity) 222 (0.2), 221 (0.8), 220 (1.2), 219 (2.7), 201 (1.6), 173 (0.6), 172 (1.6), 171 (3.7), 170 (17.6), 158 (2.7), 157 (15.7), 156 (36.2), 155 (100.0), 113 (33.7), 77 (52.4), 73 (64.6).

Anal. Sample polymerized.

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BIOGRAPHICAL SKETCH

Robert Giles Posey was born on September 18, 1947, in Plainfield, New Jersey, to Ralph T. and Amanda H. Posey. His early childhood was spent in Cranford, New Jersey, and a subsequent move to Washington, New Jersey, resulted in his completion of high school in 1965 at Washington High School. He received the degree of Bachelor of Science with a major in Chemistry from Furman University in Greenville, South Carolina in 1969, and after an additional year at Furman he completed the requirements for the degree of Master of Science, which was awarded in 1971. While at Furman, he married the former Phyllis Ann Hollingsworth of Travelers Rest, South Carolina, in 1969 and became the father of a son, Will, born on September 22, 1974. Upon completion of his studies at Furman, Mr. Posey entered the Graduate School at the University of Florida in the Fall of 1970 as a Graduate Teaching Assistant for continued study in organic chemistry. Mr. Posey is a member of the American Chemical Society.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

M. A. Battiste, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

W. M. Jones
Professor of Chemistry

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Gus J. Palenik
Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1975

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